THE CHEMICAL NEWS, January 13, 1899.

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No. 2014.—JULY 1, 1898.

ON THE COMPANIONS OF ARGON.*

By WILLIAM RAMSAY, F.R.S., and MORRIS W. TRAVERS.

FOR many months past we have been engaged in preparing a large quantity of argon from atmospheric air by absorbing the oxygen with red-hot copper, and the nitrogen with magnesium. The amount we have at our disposal is some 18 litres. It will be remembered that one of us, in conjunction with Dr. Norman Collie, attempted to separate argon into light and heavy portions by means of diffusion, and although there was a slight difference† in density between the light and the heavy portions, yet we thought the difference too slight to warrant the conclusion that argon is a mixture. But our experience with helium taught us that it is a matter of the greatest difficulty to separate a very small portion of a heavy gas from a large admixture of a light gas; and it therefore appeared advisable to re-investigate argon, with the view of ascertaining whether it is indeed complex.

In the meantime Dr. Hampson had placed at our disposal his resources for preparing large quantities of liquid air, and it was a simple matter to liquefy the argon which we had obtained by causing the liquid air to boil under reduced pressure. By means of a two-way stopcock the argon was allowed to enter a small bulb, cooled by liquid air, after passing through purifying reagents. The two-way stopcock was connected with mercury gas-holders, as well as with a Töpler pump, by means of which any part of the apparatus could be thoroughly exhausted. The argon separated as a liquid, but at the same time a considerable quantity of solid was observed to separate partially round the sides of the tube, and partially below the surface of the liquid. After about 13 or 14 litres of the argon had been condensed, the stopcock was closed, and the temperature was kept low for some minutes in order to establish a condition of equilibrium between the liquid and vapour. In the meantime the connnecting tubes were exhausted and two fractions of gas were taken off by lowering the mercury reservoirs, each fraction consisting of about 50 or 60 cubic c.m. These fractions should contain the light gas. In a previous experiment of the same kind, a small fraction of the light gas had been separated, and was found to have the density 17·2. The pressure of the air was now allowed to rise, and the argon distilled away into a separate gas-holder. The white solid which had condensed in the upper portion of the bulb did not appear to evaporate quickly, and that portion which had separated in the liquid did not perceptibly diminish in amount. Towards the end, when almost all the air had boiled away, the last portions of the liquid evaporated slowly, and, when the remaining liquid was only sufficient to cover the solid, the bulb was placed in connection with the Töpler pump, and the exhaustion continued until the liquid had entirely disappeared. Only the solid now remained, and the pressure of the gas in the apparatus was only a few millimetres. The bulb was now placed in connection with mercury gas-holders, and the reservoirs were lowered. The solid volatilised very slowly, and was collected in two fractions, each of about 70 or 80 cubic c.m. Before the second fraction had been taken off, the air had entirely boiled away, and the jacketing tube had been removed. After about a minute, on wiping off the coating of snow with the finger, the solid was seen to melt, and volatilise into the gas-holder.

The first fraction of gas was mixed with oxygen, and sparked over soda. After removal of the oxygen with phosphorus it was introduced into a vacuum-tube, and the spectrum examined. It was characterised by a number of bright red lines, among which one was particularly brilliant, and a brilliant yellow line, while the green and the blue lines were numerous, but comparatively inconspicuous. The wave-length of the yellow line, measured by Mr. Baly, was 5849·6, with a second-order grating spectrum. It is, therefore, not identical with sodium, helium, or krypton, all of which equal it in intensity. The wave-lengths of these lines are as follows:—

Na (D_1)	5895·0
Na (D_2)	5889·0
He (D_3)	5875·9
Kr (D_4)	5866·5
Ne (D_5)	5849·6

The density of this gas, which we propose to name "neon" (new), was next determined. A bulb of 32·35 cubic c.m. capacity was filled with this sample of neon at 612·4 m.m. pressure, and at a temperature of 19·92 it weighed 0·03184 grm.

Density of neon .. 14·67.

This number approaches to what we had hoped to obtain. In order to bring neon into its position in the periodic table, a density of 10 or 11 is required. Assuming the density of argon to be 20, and that of pure neon 10, the sample contains 53·3 per cent of the new gas. If the density of neon be taken as 11, there is 59·2 per cent present in the sample. The fact that the density has decreased from 17·2 to 14·7 shows that there is a consider-

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* A Paper read before the Royal Society, June 16th, 1898.

† Density of lighter portion, 19·93; of heavier portion, 20·01 (*Roy. Soc. Proc.*, vol. lx., p. 206).

able likelihood that the gas can be further purified by fractionation.*

That this gas is a new one is sufficiently proved, not merely by the novelty of its spectrum and by its low density, but also by its behaviour in a vacuum-tube. Unlike helium, argon, and krypton, it is rapidly absorbed by the red-hot aluminium electrodes of a vacuum-tube, and the appearance of the tube changes, as pressure falls, from fiery red to a most brilliant orange, which is seen in no other gas.

We now come to the gas obtained by the volatilisation of the white solid which remained after the liquid argon had boiled away.

When introduced into a vacuum-tube it showed a very complex spectrum, totally differing from that of argon, while resembling it in general character. With low dispersion it appeared to be a banded spectrum, but with a grating, single bright lines appear, about equidistant throughout the spectrum, the intermediate space being filled with many dim, yet well-defined, lines. Mr. Baly has measured the bright lines, with the following results. The nearest argon lines, as measured by Sir W. Crookes, are placed in brackets.

Reds very feeble, not measured.

First green band, first bright line	5632·5	(5651 : 5619)
,, second ,,	5583·0	(5619 : 5567)
,, third ,,	5537·0	(5557 : 5320)
Second green band, first bright line	5163·0	(5165)
,, second ,,	5126·5	(5165 : 5065) brilliant.
First blue band, first bright line	4733·5	(4879)
,, second ,,	4711·5	(4701)
Second blue band, first bright line	4604·5	(4629 : 4594)
Third blue band (first order) ..	4314·0	(4333 : 4300)
Fourth blue band (second order)	4213·5	(4251 : 4201)
Fifth blue band (first order), about	3878	(3904 : 3835)

The red pair of argon lines were faintly visible in the spectrum.

The density of this gas was determined with the following results:—A globe of 32·35 c.c. capacity, filled at a pressure of 765·0 m.m., and at the temperature 17·43°, weighed 0·05442 grm. The density is therefore 19·87. A second determination, made after sparking, gave no different result. This density does not sensibly differ from that of argon.

Thinking that the gas might possibly prove to be diatomic, we proceeded to determine the ratio of specific heats:—

Wave-length of sound in air ..	34·18
,, ,, gas ..	31·68
Ratio for air..	1·408
,, gas	1·660

The gas is therefore monatomic.

Inasmuch as this gas differs very markedly from argon in its spectrum, and in its behaviour at low temperatures, it must be regarded as a distinct elementary substance, and we therefore propose for it the name "metargon." It would appear to hold the position towards argon that nickel does to cobalt, having approximately the same atomic weight, yet different properties.

It must have been observed that krypton does not appear during the investigation of the higher boiling fraction of argon. This is probably due to two causes. In the first place, in order to prepare it, the manipulation of a volume of air of no less than 60,000 times the volume of the impure sample which we obtained was required; and in the second place, while metargon is a solid at the temperature of boiling air, krypton is probably a liquid, and more volatile at that temperature. It may also be noted that the air from which krypton has been obtained had been filtered, and so freed from metargon. A full account of the spectra of those gases will be published in due course by Mr. E. C. C. Baly.

THE SPECTRUM ANALYSIS OF SEVERAL NON-CONDUCTING MINERALS BY MELTED SALTS, AND REACTIONS OF THE ELEMENTS.

By A. de GRAMONT.

I now give a few applications of the method I have had the honour of explaining in a previous communication (*Comptes Rendus*, April 18, 1898), by which we are enabled to obtain the spectra of the lines of the elements contained in non-conducting minerals or precipitates, by exposing them, powdered and melted with an alkaline carbonate, to the action of the condenser spark.

Lithium, when tried for by using carbonate of soda, is excessively sensitive; when present even in only very faint traces it is detected by its red line 670·8, and the orange line 610·4, which may also be obtained directly in the cold by causing the condenser spark to strike on a morsel of triphane or of lepidolite.

Sodium is shown by the double red and the less refrangible double green, which will indicate quantities between 0·01 and 0·001; the double line D is always to be seen, either because of its presence in the melted salt or in the substance under examination.

Potassium is scarcely sensitive to this process. It is recognised principally by its green group, K*α* 583—578, and by its violet line 404·6, which is less characteristic, but gives a better reaction.

Rubidium, when in unweighable traces, is easily recognisable by its two violet lines 421·6 and 420·2.

Cæsium is equally sensitive by its blue lines 459·3 and 455·6.

The alkaline-earthy metals are especially easy to detect, even in very small quantities, by their principal lines, the last to disappear in the spectra; these lines are—for *calcium*, in the blue 445·5, 443·5, 442·6, and above all in the violet 442·7, as well as 396·9 and 393·4 in the ultra-violet; these last three lines we know correspond with the lines G, H, and K in the solar spectrum; for *strontium* in the blue 460·8, in the indigo 430·6, and in the violet 421·6; for *barium* in the red and orange 649·7 and 614·2, in the green 577·8, 553·6, 493·4, and in the blue 455·4.

Magnesium is recognised with great facility by the green triplet Mg*α*, which is very well known, and *glucinum* by the blue line 457·3, easy to see, but of considerably less delicacy.

Manganese, which by the direct method of analysis is not to be found, even in minerals with a metallic lustre, such as Haussmannite, is easily detected with the melted salts by its group of five blue lines, Mn*α* 482—475. The same is the case with *chromium*, which is well characterised by its triple green line 520·9, 520·6, and 520·5, the two latter being difficult to separate with a medium dispersion.

Iron and *nickel*, on the contrary, should not be sought for by this method, and if their lines are not observed it must not be concluded that the metals are not present in the body under examination.

Aluminium, the research of which is as a rule discouraged in text-books by spectrum analysis, has, on the contrary, given me a good reaction by means of its double red line 624·5, 623·5, which is brought out with great distinctness by a very small quantity of alumina in the presence of carbonate of lithium, which in this case is much preferable to the salt of soda.

Vanadium, which gives its spectrum as easily in the melted salts as in the minerals which they dissolve, shows principally by a group of strong lines in the indigo, of

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* June 16th. After fractionation of the neon, the density of the lightest same had decreased to 13·7.

which the least refrangible, 440·8, is the most persistent and the most sensitive, and which extend to 438·0.

Zirconium is easily recognised by its group of five lines between 481·6 and 469·0 in the blue; amongst these 474·0 is the strongest, and the last to disappear.

I will not dwell on the spectra of the lines of the metalloids already described in previous papers, in which I described my researches on the minerals, or in the melted salts. I will only observe that their sensitiveness, which is very great in the compounds in which they are not combined with oxygen,—such as the sulphides, selenides, tellurides, chlorides, bromides, iodides,—becomes, on the contrary, much more feeble in the corresponding oxy-salts, of which the dissociation requires a strong condensation (four to six jars) to cause the appearance of the lines of the metalloids. In this case the use of carbonate of sodium seemed to give me better results than carbonate of lithium. A certain number of minerals examined by this method have enabled me, by means of the spectral reactions I have just described, to diagnose the following elements;—

Orthose-adulaire, from Saint-Gothard and from Grisons: silicon, aluminium, potassium, sodium, barium, calcium, and sometimes magnesium.

Orthose-cassinite, from Blue Hill, U.S.A.: the same spectra, but the barium was much more developed and without magnesium.

Albite, from Modane: silicon, aluminium, sodium, calcium, magnesium.

Albite peristerite, from Villeneuve, Canada: the same spectra, with the calcium more developed.

Oligoclase, from Bakersville, U.S.A.: silicon, aluminium, sodium, calcium, barium. From Ytterby, Sweden: the same spectra, but less barium, and a stronger principal line of strontium 421·6.

Labradorite, from the coast of Labrador: silicon, aluminium, sodium, calcium.

Anorthite, from Somma and from New Caledonia: silicon, aluminium, sodium, calcium, and magnesium. The spectrum of calcium is much more developed and more brilliant than in the case of the other plagioclases, by which it is possible to distinguish anorthite at the first view of the whole spectrum.

Petalite, from Uto, Sweden: by Na_2CO_2, silicon, lithium, calcium, rubidium, aluminium (seen better with Li_2CO_3).

Pollux, from Hebron, U.S.A.: by Na_2CO_3, silicon, cæsium, lithium, calcium; and with Li_2CO_3, aluminium and sodium.

Rhodonite, from the valley of Louron, Hautes-Pyrenees: silicon, manganese, calcium, aluminium.

Beryl, from Limoges: silicon, aluminium, sodium, glucinum, calcium.

Spessartine garnet, from Saint-Marcel, Piedmont: silicon, aluminium, manganese, calcium.

Zircon, from Miask, Oural: silicon, zirconium, aluminium, calcium.

Axinite, from Oisans: silicon, aluminium, calcium, manganese, magnesium.

Garnierite (pale green), from Kanala, New Caledonia: silicon, magnesium, aluminium, but no lines of nickel, though this metal is present to the extent of 3 or 4 per cent.

Sphene, from Zermatt: silicon, calcium, titanium, aluminium.

Aerinite, from Caserras, Aragon: silicon, calcium, aluminium, magnesium, barium, vanadium.

Calc-spars: several among these have given the green triplet of magnesium and some of the lines of strontium, as well as the complete spectrum of the calcium lines.

Celestine, from Sicily: strontium, barium, sulphur with difficulty.

Siderochrome, from Silesia: chromium, magnesium, calcium. From Brousse, Asia Minor: the same spectrum and also silicon, aluminium, sodium.

Blende, from Santander and Pierrefitte: zinc, sulphur, and sometimes silver, cadmium, calcium, aluminium.

Cryolite, from Greenland: melted by itself, without the addition of any other salt, aluminium, sodium, lithium, silicon, magnesium, calcium.

This method, as can be seen, gives satisfactory results with most simple bodies, but with unequal sensitiveness. When necessary the spectrum under examination can be simplified by reducing the condenser to one jar, which will only allow of the principal lines of the metals being seen.—*Comptes Rendus*, cxxvi., No. 21, May 23, 1898.

ON THE
ANALYSIS OF BONE SUPERPHOSPHATE.
By F. POQUILLON.

The analysis of bone superphosphates is made, officially, in the same manner as that of mineral superphosphates. We estimate the phosphoric acid soluble in water, the phosphoric acid soluble in citrate of ammonia, and the total phosphoric acid.

We simply admit that the bone superphosphate should contain a higher proportion soluble in water than the mineral does, but no figures are given to show that this is the case. As a matter of fact, there is no reason for this at all, the proportion soluble in water varies with the quantity of sulphuric acid used in its manufacture; no matter whether it is bone or mineral superphosphate.

The only criterion used in deciding whether a superphosphate is bone or mineral is the estimation of the nitrogen. But this estimation does not allow of the detection of adulteration. As a matter of fact, a nitrogenous substance can easily be added to a mineral superphosphate or to a superphosphate of bone-ash to make it appear as a genuine bone superphosphate. We have recently endeavoured to find a method of controlling the estimation of nitrogen in this respect, and the following is the method we propose.

Method by the Estimation of the Fatty Matter.

This method consists in determining in a superphosphate the amount of fatty matter soluble in sulphide of carbon or in benzene, and in calculating the relation between this figure and the quantity of phosphoric acid present. This proportion is practically constant in bone superphosphates.

Green bones always have the fat removed before being transformed into superphosphates. The removal of the fat is done by two methods; by water and by benzene. Two experiments, made with each of these methods, have given the following results:—

	Total P_2O_5 per cent.	Fatty matters dissolved in benzene.	
		Per cent in bone.	Per cent P_2O_5 total.
1.	17·31	0·58	3·35
2.	17·37	0·66	3·80
Means ..	17·34	0·62	3·58

But, and here is the most important point of our method, when we treat bones from which the fat has been removed even with benzene, with sulphuric acid to transform them into superphosphates, fatty bodies are set free which are dissolved by a fresh treatment with sulphide of carbon.

We now give the results of four experiments on bone superphosphates which had had the fat removed by benzene and had then been treated with sulphide of carbon.

	P_2O_5 per cent total.	Fatty matter dissolved.	
		Superphosphate per cent.	P_2O_5 per cent total.
1.	17·10	1·14	6·67
2.	20·50	1·19	5·81
3.	17·35	1·16	6·68
4.	17·35	1·12	6·46
	19·07	1·45	6·36

If we exhaust a degelatinised bone superphosphate, from bones which have had the fat removed by water, with sulphide of carbon, we find, in addition, the fatty matter which the water has left in the bones; that is to say—

Superphosphate ..	1·15+0·62=1·77 per cent
Total P_2O_5	6·36+3·58=9·94 „

Direct determinations of the bone superphosphates generally met with, in France at least, made from bones from which the fat has been removed by water, give the following results:—

	Total P_2O_5 per cent.	Fatty matters.	
		Superphosphate per cent.	Total P_2O_5 per cent.
1. ..	17·80	2·04	11·40
2. ..	17·80	2·08	11·68
3. ..	18·40	2·24	12·71
4. ..	16·80	1·74	10·40
5. ..	16·90	1·82	10·76
6. ..	16·90	1·96	11·59
Means .	17·43	1·98	11·36

In working a superphosphate from green bones, which are also called "dissolved bones," the reaction is the same; it being, of course, understood that the fat has been removed from the bones before they are transformed into superphosphates; this should always be done commercially. In England, however, where a large quantity of dissolved bone is manufactured, the fat is not always removed; but in such cases it is bone from La Plata, the West Indies, or other tropical countries that is used, such bone rarely containing more than a trace of fat.

A direct estimation of green bones from which the fat has been removed, treated with sulphuric acid, gave the proportion of 9·68 of fatty matter per cent of the total P_2O_5.

We thus see that the proportion 10 to 12 of fat per 100 of phosphoric acid is characteristic of a superphosphate of green bones, or bones which have been degelatinised, after having originally had the fat removed by water.

The proportion 6·5 per cent is characteristic of a superphosphate from bones from which the fat has been removed by benzene.

A proportion of over 12 would indicate a superphosphate from bones from which the fat had not been removed.

From the point of view of adulteration, it may be asked if it is not possible to find a nitrogenous matter which, when added to a mineral superphosphate, could at the same time supply the necessary fat to make the characteristic proportion 10 or 12, as described above.

To decide this point, we have estimated the proportion of fatty matter in the more common nitrogenous substances and have obtained the following results:—

Material used.	Nitrogen per cent.	Fatty matters.			
		Without treating with H_2SO_4.		After treating with H_2SO_4.	
		Per cent material.	Per cent nitrogen.	Per cent material.	Per cent nitrogen.
Green horns . ..	10·94	0·58	5·30	0·39	3·56
Dried horns, No. 1	14·08	1·20	8·52	0·82	5·82
„ No. 2	13·73	0·97	7·07	0·79	5·75
Dried blood, No. 1	11·25	0·56	4·98	0·39	3·46
„ No. 2	12·65	0·45	3·56	0·37	2·93
Dried leather . ..	7·20	0·73	10·14	0·56	7·78

It will be seen from the above table that the use of these materials for the purpose of adulteration is impossible. In fact a bone superphosphate 16/18 contains from 0·75 to 1·0 per cent of nitrogen. If we take the nitrogenous matter containing the highest proportion of fat, viz., dried leather, which contains 10·14 of fatty matter per 100 of nitrogen, it is evident that to obtain 0·75 of nitrogen we have only to add $\frac{0{\cdot}75 \times 10{\cdot}14}{100} = 0{\cdot}076$ of fatty matter, while bone superphosphate contains $\frac{16 \times 11}{100} = 1{\cdot}76$.

We cannot, therefore, obtain a superphosphate containing at the same time 0·75 per cent of nitrogen and 1·76 per cent of fatty matter without using very exceptional nitrogenous material, or by adding fatty matter quite apart. Further, so small a quantity of fat (1·76 per cent of the superphosphate) could not be properly mixed in a homogeneous manner. We therefore think that our method, without being absolutely correct, will generally serve to detect cases of adulteration. — *Moniteur Scientifique*, Series 4, vol. xii., June, 1898.

THE DETERMINATION OF THE REDUCIBILITY OF IRON ORES.

By T. WIBORGH.

At the last International Congress for the unification of the methods adopted for the commercial assay of various materials, Professor J. Wiborgh, of the School of Mines at Stockholm, presented a paper on a method for the valuation of the degree of reducibility of iron ores. The following is a *resumé* of this paper:—

In the blast-furnace the reduction of an iron ore is effected both by carbon and by carbonic oxide, and it is necessary to be able to distinguish between those minerals which are easily reduced and those which are not. The former can be brought to a state of fusion with a much smaller expenditure of fuel than the latter, and this difference is largely due to the greater or less facility with which the ore gives up its oxygen to the reducing agent (carbon or carbonic oxide). This characteristic of greater or less oxidation may be compared with the greater or less ease with which carbon under different forms burns in air, — such as diamond, graphite, coke, charcoal, &c. While the combustion of diamond requires a very high temperature, the combustion of wood charcoal is, on the contrary, effected with great ease, and, as a matter of fact, takes place at a relatively low temperature. In the one case, as with the other, the difference may be ascribed to the difference in molecular structure. The density of the molecule increases with its crystalline form, the iron ore will be less easily reduced, and the carbon will be more difficult to burn, when the two substances occur in a very compact form. Furthermore, it has long been known as an accepted fact, with regard to minerals of the same degree of oxidation, that the reducibility varies inversely with the specific gravity. Any treatment which has for its object the diminution of the specific gravity is equally of value in increasing the reducibility, and it is well known that a pulverulent ore is much more easily reduced than one in compact lumps. A previous roasting, for instance, which results in the elimination of certain substances—such as water, organic matter, carbonic acid, and sulphur—also increases the reducibility of the ore by decreasing its compactness. This roasting, therefore, makes the hydrated, carbonated, and magnetic ores more easily reducible. If the peroxide of iron is more easily reduced than the magnetic oxide, it is on account of the fact that a body originally containing more oxygen gives up a part of it with greater ease. It thus follows that this first loss of oxygen breaks up the molecular structure of the substance (in the case of an ore this is obvious), and thereby its reducibility is increased. Of two ores, one of which is a peroxide and the other a suboxide of iron, the former will always be more easily reduced than the latter. The peroxide, further, possesses the property of dissociating the carbonic oxide, though under conditions which have not yet been exactly defined.

It stands to reason that, though chemical analysis enables us to determine the exact composition of an iron ore, it does not, on the other hand, supply us with any practical indication as to the greater or less ease with which such an ore will be reduced in the blast-furnace. From as far back as the year 1884 the author has been elaborating a method which had for its object the determination of this important characteristic; but this research was stopped until 1895, at which time it was taken up again at the School of Mines at Stockholm, under the direction of David Johanssen.

The apparatus used is composed of a generator of circular section, with a diameter of 0·25 metre and a height of 1·20 metres, in which an iron tube is suspended, having an internal diameter of 50 m.m.; in this tube, through which the gas from the generator passes, the samples of ore to be assayed are placed, and left there for a known time. Wood charcoal, burnt on a grate without forced draught, is the fuel used. The products of combustion are carried off by means of a pipe leading to the flue, the air entering below the grate. The actual reduction-tube terminates with a narrow end of about 35 m.m. diameter. This reduction-tube is protected from the flame by means of fire-clay; its total length is 1·60 metres, and its lower extremity is at a distance of about 250 m.m. from the hearth.

The sample of ore is crushed, and must pass through a sieve of 16 meshes per square centimetre. It is then placed in a boat of wire gauze, and suspended in the tube by means of a metallic wire. We first used 30 to 40 grms. of the mineral, but later on we made use of smaller boats not containing more than 8 or 10 grms. of the ore, three of these being placed in a larger boat at the same time. By this means several ores could be treated at one time, and comparisons made with any typical sample of iron ore.

The estimation of the temperature at which reduction takes place can be made by means of fusible alloys, or by using a thermophone invented by the author (*Chemiker Zeitung*, xx., p. 209, 1896). At 500 m.m. from the upper end of the tube the temperature is 400° C.; at 900 m.m. it is 525° C.; at 1200 m.m. it is 700° C.; and at 1500 m.m., from the same point, it is from 800° to 880° C. The proportion of carbonic acid present in the reducing gas varies from 3·2 to 3·6 per cent, and the proportion of carbonic oxide is about 30 or 32 per cent. The proportion between the CO_2 and the CO remains practically equal to 0·1. If the lower end of the tube is raised by 350 m.m. from the furnace, the proportion of carbonic acid in the gas is increased to 17 per cent.

The assay may be carried out in two distinct manners,—by allowing the boat to gradually descend to the warmest part, or by placing it there at once. But as it is necessary to take into account the separation of the carbon which occurs at about 400° by dissociation of the reducing gas, and as, on the other hand, this dissociation is of considerable importance in the reduction of the mineral, it is preferable to adopt the former method. We can also—and this is an excellent plan—leave the ore at a temperature of 400° for one hour, and then lower the boat directly into the hottest part of the tube, where it can be left for another hour. The experiments which will be described further on were conducted in this manner.

When the reduction is complete it is necessary to be careful to allow the boats to cool in a current of carbonic oxide, so as to prevent the re-oxidation of the metallic iron obtained. There then remains the analysis of the reduced ore to be done, and this will offer considerable difficulty if the reduction has not been complete, or if the metallic iron is mixed with oxide.

The possible proportion of oxygen remaining in the ore after reduction is calculated under the *term, degree of oxidation of the iron*. This degree of oxidation is the proportion (in units per cent) of the oxygen found after reduction, to the amount of oxygen which would be found if the whole of the iron present was in the state of peroxide. Under such conditions we take *the degree of oxidation* of peroxide of iron to be 100, that of the magnetic oxide 88·9, and that of the suboxide 66·7. Finally, it must be borne in mind that the quantity of carbon present in the ore, after reduction, must be estimated. The characteristics, therefore, to determine are:—(1) carbon; (2) total iron; (3) metallic iron; (4) degree of oxidation.

A. *Estimation of the Carbon.*

For this purpose we use Särnström's apparatus as used for the estimation of the carbon in cast-iron. The oxidation is carried out by the chromic solution, and the absorption of the carbonic acid by means of potash.

B. *Estimation of the Metallic Iron.*

The reduced sample is treated with sulphuric acid, and the hydrogen collected. The measurement of the volume of the gas will enable one to calculate the metallic iron present. For this estimation we make use of a large-sized test-tube, in which is placed from 0·2 to 1·0 grm. of the sample, according to whether it is more or less completely reduced. This tube must be closed by means of an indiarubber stopper pierced with two holes, through which pass respectively the tube of a funnel and an escape-tube. The funnel is used for the admission of sulphuric acid. The escape-tube is for the purpose of leading the hydrogen given off to a potash wash-bottle, in which all traces of carbonic acid gas which might be present, if the ore had been insufficiently roasted, would be absorbed. After this washing, the hydrogen passes into a graduated burette, of which the lower extremity is connected to a hot-water oven. The sample is first placed in the test-tube, a little water is then added, and the cork inserted. The exact level must now be established between the water oven and the burette, after which exactly 10 c.c. of dilute sulphuric acid (one part of acid to eight parts of water) is run into the test-tube. When the reaction appears to be finished the test-tube is warmed and kept at the boiling-point for a few moments. The level must now be again adjusted, the burette cooled down to 20° C. (this should also have been done at the commencement), and the volume of the gas read off, from which the quantity of acid introduced may be calculated. All these details are not actually insisted upon, but they will always be found worth notice in a gas analysis.

The reaction which takes place is the following:—

$$Fe + H_2SO_4 = FeSO_4 + H_2.$$

Now 1 litre of hydrogen at 0° C., at a pressure of 760 m.m. of mercury, weighs 0·08957 grm.; therefore 1 grm. of iron will give $\frac{2 \times 0{\cdot}1 \times 1000}{56 \times 0{\cdot}08957} = 39{\cdot}8$ c.c. of hydrogen at a temperature of 0°, and at the normal pressure. At 20° C. the volume of the hydrogen will be 42·7 c.c.

This figure has further been verified experimentally by the use of samples of iron containing variable amounts of carbon. The following are the results obtained:—

0·1 grm. of iron with 0·08 per cent of carbon gave 42·4 c.c. of hydrogen.
0·1 grm. of iron with 0·34 per cent of carbon gave 41·4 c.c. of hydrogen.
0·1 grm. of iron with 0·78 per cent of carbon gave 41·2 c.c. of hydrogen.
0·1 grm. of iron with 3·80 per cent of carbon gave 34·8 c.c. of hydrogen.

From the above it may be seen that with irons containing a high percentage of carbon the gaseous volume is distinctly diminished, because of the formation of carbides of hydrogen. But as a matter of fact this particular point has not much bearing on the class of assays with which we are now concerned, since the iron reduced by the method just described would never contain more than a trace of carbon. The only loss of hydrogen which might occur would be caused by the action of this gas on the ferric salt in solution (*i.e.*, by the formation of the ferrous salt and water).

C. *Estimation of the Total Iron.*

0·25 grm. of the sample is attacked with hydrochloric acid, filtered, and transformed into sulphate by evaporation with sulphuric acid. This is taken up with water, reduced by the action of zinc, and the iron titrated with permanganate.

D. *Determination of the Degree of Oxidation.*

0·4 of the sample is placed in an emery-stoppered test-tube, having only a very small orifice. To begin with about 5 c.c. of a 10 per cent solution of sulphuric acid is added, and the whole left at the ordinary temperature, but frequently shaken. Complete solution takes from thirty to sixty minutes. When all disengagement of gas has ceased, about 5 c.c. of sulphuric acid, of 1·23 density, are added, and the solution warmed until the whole of the iron is dissolved. This solution is then poured into a beaker and titrated with permanganate.

In the case of refractory ores which are not easily attacked, the first liquor obtained by the action of the dilute acid must be separated by decantation, and the undissolved residue submitted to a fresh attack by a more concentrated acid. The two solutions must then be added together for titration. Having thus obtained the whole of the iron contained in the sample of the ore, and having determined by the preceding assays the quantity of metallic iron and the quantity of iron in the state of suboxide, it is a matter of comparative simplicity to calculate the degree of oxidation. Thus let n % be the total iron present, and r % the proportion of metallic iron, and m % the quantity of iron present in the state of suboxide, then the degree of oxidation is arrived at by means of the following formula:—

$$\frac{\frac{(n-r)\,3}{2}}{m-r} + \left[\frac{(n-r) - (m-r)}{2}\right]3 = \frac{100}{x},$$

from which we get:—

$$x = \text{the degree of oxidation} = \frac{1 - \frac{m - r}{3(n-r)}}{100}.$$

The formula for the peroxide of iron, Fe_2O_3, may very well be written Fe_6O_9. It can be shown that this compound may successively lose 4 molecules of oxygen, which will correspond to the following four different oxides:—

	Degree of oxidation.
$3Fe_2O_3 = Fe_6O_9$	100·0 oxide.
$3Fe_2O_3 - O = Fe_6O_8$ ..	88·9 suboxide of the oxide.
$3Fe_2O_3 - 2O = Fe_6O_7$ ..	77·8 oxide of the suboxide.
$3Fe_2O_3 - 3O = Fe_6O_6$ ..	66·7 suboxide.

E. *Determination of the Degree of Reduction.*

The real estimation of the reducibility is given by the *degree of reduction*,—that is to say, by the relation between the iron reduced and the total iron present (in units per cent).

The experiments which have been carried out by the method above described, on thirty-six samples of ores, have shown that the peroxidised minerals are more easily reduced than those of the magnetite class. This difference has, however, long ago been established in practice. But there is another point which must not be lost sight of,—that these experiments on the reducibility of iron ores also show that the oxidation point may vary in a marked degree. And it may well be hoped, from the above-mentioned facts, that a simple and practical method for the rapid evaluation of the comparative reducibility of any iron ore may be easily arrived at.

It must be taken as an established fact that between peroxide of iron and metallic iron there exists a complete series of intermediary states, which are, and must be, determined by the action of the reducing agents. To particularise, the existence of the suboxide of the oxide ($Fe_3O_4 = Fe_6O_8$), of which the degree of reducibility is 88·9, was shown by Ackerman in the year 1882. Still more important, from the point of view of reduction, is the oxide of the suboxide, Fe_6O_7, of which the existence was shown by Wedding. The degree of oxidation of this body is 77·8.

From a careful consideration of all the experiments carried out by the author, the following conclusions may be drawn:—Every mineral giving a degree of oxidation of 77·8, at a low temperature, will be easily reducible,—that is to say, it can be transformed into metallic iron by the ordinary furnace gas. This degree of oxidation corresponds to a particular and definite molecular condition, by reason of which there is not a particle of metallic iron formed until it has been reached. As soon, however, as this point *has* been reached the reduction proceeds very rapidly, at the same time *the degree of oxidation* diminishes, but, contrary to the belief of most metallurgists, the suboxide or the protoxide of iron does not constitute a "molecular step" in the reduction of the ore.—*Moniteur Scientifique*, Series 4, vol. xii., June, 1898.

DETERMINATION OF TEMPERATURE BY MEANS OF THE DATA GIVEN IN A CHARLOTTENBURG CERTIFICATE.

By A. W. WARRINGTON, M.Sc.

Although it must be pretty generally known in England that thermometers obtained from Germany may, for a few extra shillings, be examined at Charlottenburg and furnished with a certificate giving, to the one-hundredth of a degree, the corrections to be applied at various points, I doubt whether we sufficiently avail ourselves of this privilege, or are aware of the extreme trustworthiness of results obtained by use of such a certificate.

A thermometer, designated in this paper by T 9591, made of normal Jena glass and divided into tenths of a degree, was examined by me after the manner recommended by M. Guillaume in his "Traité Pratique de la Thermométrie," its fundamental interval being determined by comparison at several points with a thermometer, T 11806, made by Tonnelot and examined at the Bureau International des Poids et Mesures.

T 9591 was furnished with a Charlottenburg certificate, by means of which its readings might be reduced to those of the standard gas thermometer at Charlottenburg. This standard is, for the purpose of this paper, treated as identical with the "Paris" hydrogen standard.

To use the Charlottenburg certificate, the zero of the thermometer, after prolonged exposure to the temperature of the room, should be determined. Let the zero be x; then, if the thermometer be used in a vertical position and the whole of the column of mercury be exposed to the temperature to be measured, the following, according to the Charlottenburg certificate, are the only corrections which need be applied to reduce the readings of T 9591 to the standard gas thermometer.

At	0°	add	$-x$
,,	10°	,,	$-x-0{\cdot}02°$
,,	20°	,,	$-x-0{\cdot}02°$
,,	30°	,,	$-x-0{\cdot}05°$
,,	40°	,,	$-x-0{\cdot}01°$
,,	50°	,,	$-x-0{\cdot}04°$

The corrections for intermediate temperatures being determined by Broch's method of interpolation.

The comparisons given in the accompanying table

$-x$.	T 9591 unreduced.	T 9591 reduced by Charlottenburg certificate.	T 9591 reduced by method employed at Sèvres.	Th.* obtained from T 11806.	Charlottenburg −Th.*	Sèvres −Th.*
+0·161	14·2575	14·3985	14·3963	14·3945	+0·004	+0·0018
+0·161	37·0062	37·1462	37·1490	37·1472	−0·001	+0·0018
+0·161	25·4190	25·5410	25·5497	25·5501	−0·009	−0·0004
+0·161	29·7695	29·8805	29·8834	29·8877	−0·007	−0·0043
+0·161	40·8040	40·9530	40·9485	40·9473	+0·006	+0·0012
+0·140	9·6215	9·7445	9·7486	9·7490	−0·005	−0·0004
+0·140	9·028	9·150	9·1574	9·156	−0·006	+0·0014
+0·140	8·038	8·162	8·1640	8·163	−0·001	+0·0010
+0·140	6·388	6·515	6·5193	6·516	−0·001	+0·0033
+0·140	4·7188	4·8488	4·8448	4·8444	+0·004	+0·0004
		Probable error of a determination			±0·004	±0·0014

* Th = T according to the hydrogen standard at Sèvres.

illustrate the method and the degree of accuracy obtainable.

In conclusion, the Charlottenburg certificate costs only a few shillings; by its means reductions are made with the greatest ease, and, if the bore of the thermometer is a good one, the reductions are correct to 0·01°.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 16th, 1898.

Professor DEWAR, F.R.S., President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. Edward Gardner, 27, Thurlow Road, Hampstead, N.W.; Henry J. S. Sand, 2, Cantlowes Road, Camden Square, N.W.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—

Harry Brearley; Arthur William Cowburn; Charles W. Tisdale Davies; Edwin Dowzard; A. Grant Russell Foulerton; Oswald Hamilton; A. Stanley Hemmy, B.A., M.Sc.; Robert Findlay Hislop; George Arthur Jarvis; Harry Lancelot Lee; William Lewins, B.Sc.; George Herbert Martin, B.A.; Charles James Meads; Leonard Myddleton Nash; Alex. MacGillivray Neilson; Edward John Russell, B.Sc.; Matthew Joseph Sheridan; Sigmund Stein, Ph.D.; Oscar Julian Steinhart, Ph.D.; Samuel Auchmuty Tucker, Ph.B.; Henry Trench Waller; Frank Edwin Weston; Edmund Thomas Whitaker, B.Sc.; William Ernest Wild, B.Sc.; William Williamson; Ernest Witham; Charles Arthur Wrench.

Of the following papers those marked * were read:—

*86. "*Preparation of a Standard Acid Solution by Direct Absorption of Hydrogen Chloride.*" By G. T. MOODY.

A very rapid and accurate method of preparing a standard acid solution consists in absorbing hydrogen chloride in water, determining the resulting increase in weight, and subsequently diluting to a suitable bulk. The absorption is conveniently carried out in a conical glass flask, having a capacity of about 80 c.c., and closed by a glass stopper. Through the stopper pass two tubes, one of which reaches nearly to the bottom of the flask and serves for delivery of the gas. From 2 to 4 grms. of the gas may be absorbed in 40 c.c. of water in three minutes, and if the necessary apparatus for generating hydrogen chloride is kept fitted, a standard acid solution can be prepared in less than fifteen minutes.

*87. "*Researches on the Terpenes. III. Halogen Derivatives of Fenchene and their Reactions.*" By JOHN ADDYMAN GARDNER, M.A., and GEORGE BERTRAM COCKBURN, B.A.

The authors give a further account of the properties of chlorofenchenephosphonic acid, $C_{10}H_{14}Cl\cdot PO(OH)_2$ (*Trans.*, 1897, lxxi., 1156), and describe the halogen derivatives of fenchone produced during its formation. The first action of phosphorus pentachloride on fenchene results in the replacement of the oxygen atom by chlorine, and production of two isomeric liquid substances, termed α- and β-chlorofenchene hydrochloride. These two isomerides cannot be separated by fractional distillation, but distil together at 105—110° under 16 m.m. pressure. The α-isomeride is, however, very much the less stable of the two, and loses hydrogen chloride very readily, even when distilled with steam, producing chlorofenchene. The β-isomeride is much more stable towards reagents, and does not lose hydrogen chloride by boiling with aniline; this elimination can be effected, however, by prolonged heating with zinc dust and glacial acetic acid, and chlorofenchene is obtained. Unlike the chlorocamphene hydrochlorides, β-chlorofenchene hydrochloride is completely decomposed by warming with strong sulphuric acid, and yields no substance analogous to camphenol.

Chlorofenchene, $C_{10}H_{15}Cl$, is a crystalline substance very like chlorocamphene in appearance. It boils at 80—83° under 16 m.m., and at 190—192° under the ordinary pressure. It is very soluble in alcohol, ether, benzene, light petroleum, chloroform, and carbon disulphide, the vapour of the last being sufficient to liquefy it. It has a specific rotatory power of $[\alpha]_D = +35\cdot92°$. Chlorofenchene slowly reacts with phosphorus pentachloride, and chlorofenchenephosphonic acid is formed on treating the product with water.

When sodium chlorofenchenephosphonate is treated with bromine water, it is decomposed quantitatively into sodium phosphate and *chlorobromofenchene*, $C_{10}H_{14}ClBr$; this is a colourless oil which boils at 113—114° under 11 m.m., but decomposes on boiling under atmospheric pressure. It has a specific gravity of 1·38039 at 16°, and a specific rotatory power of $[\alpha]_D = -8\cdot42°$. The halogen atoms cannot be eliminated by heating with aniline, with zinc dust and glacial acetic acid, or with sodium in methylic alcohol solution.

*88. "*Researches on the Terpenes. IV. On the Oxidation of Fenchone.*" By JOHN ADDYMAN GARDNER and GEORGE BERTRAM COCKBURN.

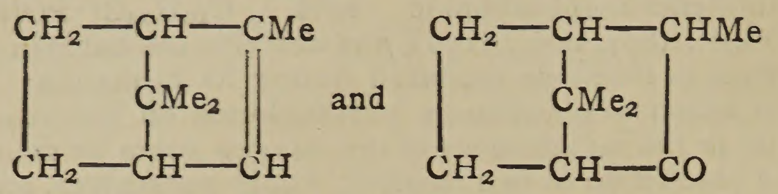
Fenchone is much more stable towards oxidising agents than camphor, but when oxidation does take place a much more complete breaking down of the molecule occurs. The authors have oxidised fenchone by prolonged heating on the water-bath with concentrated nitric acid (sp. gr. 1·4). The action was very slow, and after heating for a week, they found that only about 50 per cent of the ketone had been attacked. Isocamphoronic acid, dimethyltricarballylic acid, dimethylmalonic acid, isobutyric acid, acetic acid, and nitrofenchone were isolated from the product of oxidation.

The isocamphoronic acid crystallised from ether and ethylic acetate in tabular plates melting at 163—164°, and is identical with the isocamphoronic acid obtained by Tiemann from campholenic acid. The yield was about 1·5 per cent of the weight of the fenchone actually oxidised.

The dimethyltricarballylic acid melted at 155°, and on treatment with acetic chloride gave an anhydride melting at 139—141°. The triethylic salt was a colourless liquid and boiled at 172—174° under 19 m.m. pressure. The lead salt, $(C_8H_9O_6)_2Pb_3$, was an insoluble powder. The yield of this acid was 30 per cent, and of dimethylmalonic acid 4 per cent of the fenchone oxidised.

Nitrofenchone is a colourless oil which distils at 146—151° under 14 m.m. pressure, and on reduction with stannous chloride is converted into an amine.

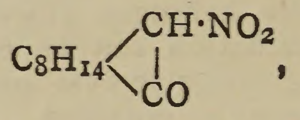
The authors are of opinion that if Bredt's formula be accepted for camphor, these results, taken together with the production of camphopyric acid from fenchene without the intermediate formation of camphoic acid, and from camphene, are sufficient to establish the formulæ—



for fenchene and fenchone respectively.

*89. "*Nitrocamphor and its Derivatives.* Part I. *Isodynamic Forms of Nitrocamphor.*" By T. M. Lowry, B.Sc.

Although, theoretically, it should be possible to obtain two stereoisomerides of a compound represented by the formula—

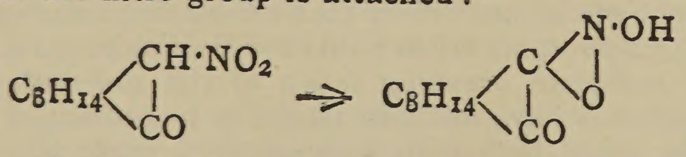


$$C_8H_{14}\left<\begin{matrix}CH\cdot NO_2\\ |\\ CO\end{matrix}\right. ,$$

it appears that only one (the α') of the two possible forms of nitrocamphor is produced under all ordinary conditions, since the various substances described as isomeric nitrocamphors have been found by the author to have the same properties when sufficiently purified.

The product obtained by heating nitrocamphor (*Proc.*, 1897, xiii., 169) has the formula $C_{20}H_{28}N_2O_5$, and is identical with a substance already described by Cazeneuve as nitrosocamphor (*Bull. Soc. Chim.*, 1888, iii., I., 558); it appears to be an *anhydride* formed by the removal of the elements of a molecule of water from two molecules of nitrocamphor, or rather of an isodynamic form of the latter which may be termed pseudonitrocamphor. This view finds support in the fact that the anhydride, like the salts formed from nitrocamphor, is strongly dextrorotatory, whereas nitrocamphor is lævorotatory; and that when heated or acted upon by alcoholic potash, it breaks up into camphorquinone and nitrous oxide, undergoing a change analogous to that which Nef has shown to take place on acidifying a solution of sodium ψ-nitroethane (*Annalen*, 1894, cclxxx., 263).

If pseudonitrocamphor be represented by a formula corresponding to that which Hantzsch and Schultze have assigned to pseudophenylnitromethane, rather than by an isonitro-formula such as Nef has proposed, it is obvious that the conversion of nitrocamphor into the isodynamic form would not affect the asymmetry of the carbon atom to which the nitro-group is attached:—

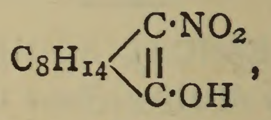


$$C_8H_{14}\left<\begin{matrix}CH\cdot NO_2\\ |\\ CO\end{matrix}\right. \rightarrow C_8H_{14}\left<\begin{matrix}C\left<\begin{matrix}N\cdot OH\\ |\\ O\end{matrix}\right.\\ |\\ CO\end{matrix}\right.$$

The author considers that important evidence of the independent existence of pseudonitrocamphor is afforded by the fact that solutions of nitrocamphor exhibit the phenomenon of multirotation hitherto observed only in the case of carbohydrates. This is true of $\pi\alpha'$-bromonitrocamphor, in which the group $-CH(NO_2)\cdot CO-$ is also present, but not of $\alpha'\alpha$-nitrochlorocamphor, $\alpha'\alpha$-nitrobromocamphor, nor of the anhydride or salts obtained from nitrocamphor, from all of which the hydrogen atom contiguous to the nitro-group has been eliminated. The extent to which the rotatory power of nitrocamphor changes corresponds to the formation of from 5 to 10 per cent of the pseudo-form in solution.

It has not been found possible to isolate pseudonitrocamphor as yet. In the case of $\pi\alpha'$-bromonitrocamphor, however, three different crystalline forms are known. The author is of opinion that the orthorhombic modification melting at 142°, which has a specific rotatory power changing from +189° to −40° in a 3·33 per cent benzene solution, is the pseudo-form, and that the tetragonal form melting at 186°, which has a specific rotatory power changing from −50° to −40°, is the pure normal $\pi\alpha'$-bromonitrocamphor. The third microcrystalline modification, melting at 126°, appears to be composed of the two isodynamic forms in the ratio of one part of the normal to about five of the pseudo-compound. Equilibrium is attained in solution by all the three modifications at a point corresponding to the presence of only about 4 per cent of the pseudo-compound; the fact that this form is nevertheless the one most readily obtained on crystallisation is not difficult to account for as it is much less soluble than the normal compound.

The camphornitrophenol which Cazeneuve obtained by the action of concentrated muriatic acid on nitrocamphor obviously represents a third form of isomerism, as it behaves as a saturated compound and shows phenolic properties. Its behaviour is not explained by the formula,—



$$C_8H_{14}\left<\begin{matrix}C\cdot NO_2\\ \|\\ C\cdot OH\end{matrix}\right. ,$$

proposed by Cazeneuve, since this represents it as being merely the enolic form of nitrocamphor. A change similar to that produced by hydrogen chloride occurs when benzoyl chloride acts on an alkaline solution of nitrocamphor, the product being camphornitrophenol benzoate. Cazeneuve has suggested that the formation of camphornitrophenol is due to the addition and subsequent loss of a molecular proportion of hydrogen chloride; it is possible that benzoyl chloride acts in a similar way by forming an additive compound from which hydrogen chloride is subsequently removed. The author is engaged in studying camphornitrophenol as well as its isomerides with a view of determining their inter-relationships.

*90. *Cannabinol.*" By T. B. Wood, M.A., W. T. N. Spivey, M.A., and T. H. Easterfield, M.A., Ph.D.

Notwithstanding the experimental evidence already adduced by the authors in favour of the homogeneity of cannabinol (*Trans.*, 1896, lxix., 539; *Proc.*, 1898, xiv., 66), further investigation has shown that the substance is a mixture.

The crystalline acetyl derivative to which the formula $C_{15}H_{18}O_2$ was assigned (*Proc.*, *loc. cit.*) is found by molecular weight determinations to possess the formula $C_{23}H_{28}O_3$, which has the same percentage composition. This conclusion is supported by the determination of the acetyl and by the examination of the other product of hydrolysis, which has the composition and molecular weight required for the formula $C_{21}H_{26}O_2$. Most of the samples of cannabinol examined have yielded about 20 per cent of the crystalline acetyl compound, together with an oily acetyl derivative containing a lower percentage of carbon.

The compound $C_{21}H_{26}O_2$ boils at 280—290° under 80 m.m. pressure. When dissolved in glacial acetic acid and treated in the cold with fuming nitric acid, it yields a bright yellow crystalline *nitro*-derivative, $C_{21}H_{23}N_3O_8$, which is more conveniently obtained by the action of nitric acid on cannabinol under similar conditions, the yield amounting to 20 per cent of the cannabinol used. This nitro-derivative melts at 160° with decomposition, has acid properties, and gives characteristic *ammonium*, *potassium*, and *silver* salts which are sparingly soluble in water, but dissolve easily in alcohol, and have the general formula $C_{21}H_{22}N_3O_8M$. The *sodium* salt is comparatively soluble and crystallises with four molecular proportions of water. On reduction, the nitro-compound yields a corresponding base. Hot fuming nitric acid oxidises the nitro-compound to nitrocannabinolactone (oxycannabin), a mixture of acids being produced at the same time.

Amidocannabinolactone, $C_{11}H_{11}NH_2O_2$ (*Proc.*, *loc. cit.*), has been diazotised and converted into a crystalline *iodolactone*, $C_{11}H_{11}IO_2$, which melts at 137·5° and can be sublimed. On removal of iodine from this compound by the action of sodium amalgam an oily lactone is obtained.

*91. "*An Improved Form of Gas-analysis Apparatus.*" By WILLIAM A. BONE.

The author has devised an improved form of gas-analysis apparatus, suitable for all purposes where considerable accuracy in estimating small quantities of gases is required.

The apparatus consists essentially of—(1) A measuring vessel, A, made in one piece with a barometer tube, B. Both A and B are 700 m.m. long, and have the same internal and external diameters, viz., 15 and 17 m.m. respectively. B is very accurately graduated into millimetres. A and B are enclosed in a rectangular water-jacket, through which a stream of water at a constant temperature can be made to flow, and are connected by means of special steel joints and a steel tap to a movable mercury reservoir. (2) A laboratory vessel standing in a mahogany trough over mercury, into which the gases can be sent for absorption purposes. (3) An explosion vessel, similar to but rather larger than that of the Dittmar apparatus, in which all explosions are carried out.

The measuring vessel is provided with a three-way glass tap having two parallel capillary branches, one of which goes to the laboratory vessel, the other to the explosion vessel; the junctions are rendered vacuum tight by a device of steel faces and a clamp similar to that introduced by Regnault.

The moist gases are measured by bringing them to a certain constant volume in A, and then deducing their tension in terms of millimetres of mercury from the reading on the barometer, B. Since the gases in A are moist, and the "vacuum" in B is always kept saturated with water vapour, it is obvious that, provided the temperature of the water surrounding A and B remain constant throughout an analysis, none of the usual corrections for temperature, tension of water vapour, &c., need be applied to the analytical figures, as differences in readings on the barometer, under these conditions, correspond to differences in volume in the gases measured.

DISCUSSION.

Prof. MCLEOD thought that too much credit was ascribed to him for the gas-analysis apparatus, which was only a modification and simplification of that devised by Sir Edward Frankland. He had done away with the centre filling tube, so that a narrower glass cylinder which could be closed by an indiarubber plug was sufficient, thus avoiding complicated metal work; he had also lengthened the barometer, and thought that the author diminished the accuracy of his apparatus by making the barometer and measuring tube of the same length. All the stopcocks were made of glass, which seemed preferable to steel, as any leakage could be more easily detected and remedied. One small part of the apparatus he did claim, and that was the suspended globular mercury reservoir, and he was gratified to see that this simple device was in use in very many forms of apparatus in which mercury is employed.

Mr. G. N. HUNTLY said that he had been working for some time with a slightly modified form of the Frankland apparatus, in which the black glass points of Joly were used instead of lines etched round the tube. The accuracy of this method of reading is so great that a tube of 1 inch diameter can be used without loss of precision. The author's experience with the Dittmar-Lennox pipette did not agree with his own, as experiments made with a view of testing these pipettes showed that 5 c.c. of gas, measured initially at atmospheric pressure, could be transferred backwards and forwards repeatedly without the readings on the barometer tube differing by more than 0·1 m.m., an accuracy of 1 in 7000. With careless working, transference tended, not to a loss of gas as the author suggested, but to a gain, minute air bubbles being introduced apparently from the fingers.

*92. "*Preliminary Note on the Action of Light on Acetylene.*" By WILLIAM A. BONE and JOHN WILSON.

Some time ago the authors noticed that acetylene undergoes a well-marked change on exposure to bright sunlight. Tubes of about 100 c.c. capacity, drawn out at each end and terminated by capillary glass taps, were filled at atmospheric pressure with pure acetylene prepared from copper acetylide, and dried by passing through a concentrated solution of potassium hydroxide. Some of these tubes were exposed on the roof of the laboratory throughout June and July of last year, when the weather was particularly fine. After two or three days' exposure, a faint brown deposit was observable on the inside of the bulbs. This gradually increased in extent and thickness until, at the end of a fortnight, the tubes were entirely covered with a dark brown greasy deposit. The change was evidently due to the action of sunlight, for if a portion of the tube were screened from the light no deposit was formed over the area so protected, and, further, after the tube had become coated with the opaque deposit no further action was noticeable, even after prolonged exposure. Acetylene was decomposed to a less extent when exposed in tubes during August and September, 1897, than during the previous two months. The decomposition is independent of the presence of air, because acetylene mixed with its own volume of oxygen or nitrogen was exposed to sunlight for a very long period without any appreciable change occurring.

A slight contraction in volume was observed when tubes exposed during last summer were opened over mercury. A measured quantity of the gas sent into a Hempel pipette containing a freshly prepared ammoniacal solution of cuprous chloride was quickly reduced to about 2 per cent of its original volume. The residual gas, after treatment with dilute sulphuric acid, appeared to contain a fairly dense hydrocarbon absorbed by fuming sulphuric acid, mixed possibly with a small quantity of hydrogen; no saturated hydrocarbon could be detected.

The solid deposit on the side of the tube was removed by treatment with fuming nitric acid, in which it does not dissolve to any appreciable extent. On removal of the acid by filtration, irregular yellow plates remained. The acid filtrate was carefully tested for the presence of nitro-derivatives of benzene and naphthalene, but without success. The yellow plates were insoluble in hot benzene, and could be heated at 270° without melting or undergoing any change; they apparently consisted of a very dense hydrocarbon or hydrocarbons.

The authors are working this summer on larger volumes of acetylene, and hope eventually to determine the nature of the products obtained.

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, June 24th, 1898.

Mr. WALTER BAILY in the Chair.

PROF. CARUS-WILSON exhibited an apparatus to illustrate the action of two electric-motors coupled in such a way as to admit of their rotating at different speeds. The two shafts are placed in line, and each is fitted with a bevel-wheel gearing into an intermediate wheel. The axis of the intermediate wheel is at right angles to the line of the motor-shafts, and is free to rotate in a plane at right-angles to that line. The motors can be made to rotate at different speeds by altering the strength of the magnets of either or both. The motion of the intermediate wheel depends upon the difference of the two speeds, or upon their mean, according to their relative directions of rotation. A simple graphic construction enables the action to be pre-determined for any given load on the intermediate wheel. Calling the two motors A and B, and the intermediate wheel C, lines can be drawn on a base of current, to represent the speeds and the torques for each motor. If the motions of A and B are in the same direction, the load or torque is the same on each, and of similar sign. Hence, as the load on the wheel C is increased, the speeds of A and B tend to become equal (if A had been running faster than B); and for a certain load on C the speeds of A and B will be equal. If the load on C is further increased, B will run faster than A. Also, there will be a certain value for the load on C at which the motion of A will reverse. A further increase of the load on C will bring C to rest, A and B then rotating at equal speeds in opposite directions. When the load on C is nothing, let the motors rotate in opposite directions, A running faster than B. The motion of C now depends upon the difference of speeds of A and B. When a load is put on C, the motion of A is retarded, while that of B is assisted; hence B takes less current, and A takes more. The torques on the two motors, due to the load on C, are now of equal amount, but of opposite sign. As the load on C is increased, the speed of A is reduced, and that of B increased, until the two are equal and C comes to rest. B is now acting as a generator, and sending current into A. If the load on C is simply that due to friction, the process cannot be carried further. But if the load on C is reversed, the speed of B becomes greater than that of A, and the motion of C is reversed. In the steering gear designed by the Union Electricitäts Gesellschaft, the intermediate wheel is made to actuate a rudder, by differential action. The motion is reversed by making the speed of one motor greater or less than that of the other.

Mr. Quick then exhibited Weedon's apparatus for the measurement of the expansion of solids. This method is claimed to be independent of knowledge of optics on the part of the student. The expansion is read directly by means of a pair of micrometers. Precautions are taken to prevent errors due to radiation.

Mr. Lehfeldt asked what precautions were taken to prevent the movement of the micrometer supports.

Mr. Stansfield described a form of apparatus in use at Chelsea Polytechnic; it was a simple contrivance, in which changes of length were measured by a micrometer.

Mr. Quick, replying, thought the instrument referred to by Mr. Stansfield pre-supposed a knowledge of optics.

Mr. Lehfeldt then read a paper, by Dr. Donnan, on the "*Theory of the Hall Effect in a Binary Electrolyte.*"

In 1883 Roiti investigated the subject of a possible Hall effect in electrolytic solutions. He failed to obtain any positive result. Recently the question has been examined by Bagard, who noticed certain effects in aqueous solutions of zincic and cupric sulphates. Meanwhile negative results have been observed by Florio. The author therefore discusses what effect might be expected by theory, on somewhat the same lines as those of Van Everdingen, Jr., taking a more general case. So far as the present discussion goes, the author's theory is wholly in favour of the negative results of Roiti and Florio. It would appear that Bagard measured a phenomenon not contemplated by the theory as stated in the present treatment. Van Everdingen originally supported the positive results of Bagard; but his work, unfortunately, was rendered incorrect by the accidental omission of a numerical factor. He has since discovered the slip in his calculations, and now agrees with the author's conclusions.

The Chairman proposed votes of thanks to the authors, and the meeting adjourned until October, this being the last of the Session.

NOTICES OF BOOKS.

The Kinetic Imagining of Gases. (An Open Letter). By Stephen H. Emmens. New York.

We are in receipt of a remarkable pseudo-scientific pamphlet bearing the above title. Considering its shortness it contains a wonderful collection of errors and fallacies, and shows considerable internal evidence that the author has either had no scientific training or has not known how to profit by it.

The subject of the pamphlet is a crude attack on the Kinetic Theory of Gases, and on the people who believe in it; but we are of opinion that the theory in question is sufficiently firmly established to withstand more formidable assaults than this.

The author, after appealing to the scientific public for careful consideration, opens by describing half an experiment, and asking them to draw a whole conclusion from it. This is an error which, we trust, none but novices, and but few of them, will fall into.

In the next place, he challenges the world to adduce a single observed fact in proof of the Kinetic Theory of Gases. This is a well-known schoolboy method of arguing. Might we gently hint, however, to the author that, since he is attacking an accepted theory, the onus of proof lies with him?

His next remark is even wilder, for he quotes the cathode rays as not behaving according to theory. May we ask which theory? There are several provisional theories to choose from, though neither is generally accepted.

He then goes on to invite all who are desirous of seeing error replaced by truth—a laudable desire—to aid in collecting natural facts showing the Kinetic Theory of Gases to be but a vain imagining. We need hardly point out that any one who enters on a research with a preconceived idea of what the result is to be, is likely to arrive at an untrustworthy conclusion, and must not be surprised if a critical public declines to accept it at its face value.

He concludes by drawing attention to the bad reception which Charles Darwin's theory of the Origin of Species met with when first it was propounded, and infers that every new theory which is badly received by scientific men is, *ipse facto*, true. The fallacy involved is apparent.

We would point out to the author that the first requisite of a scientific man is an open mind; the second is the skill to perform careful and accurate experiments and record them correctly; and the third is the ability to draw correct conclusions from them: the pamphlet under review offers no evidence that he is possessed of any one of them.

OBITUARY.

Dr. A. D. van RIEMSDIJK.

In the twenty-eighth Annual Report of the Deputy Master of the Mint, just issued, we find a fitting tribute to the memory of the late Dr. van Riemsdijk, Director of the Utrecht Mint, which occurred on the 26th of April last, when Holland lost an eminent chemist. He was one of a small band of scientific workers who, some forty years ago, influenced by the late Prof. Stas, conducted elaborate investigations with a view to improve the operations of coinage. The results of his own researches not only contributed to accuracy in assaying, but have been of material service in connection with certain chemical operations which are conducted in Mints. He was an excellent chemist, and always ready to assist his *confrères* with his advice. These few words are offered in sincere appreciation of the value of his labours.

CORRESPONDENCE.

THE NEW GASES.

To the Editor of the Chemical News.

Sir,—If Mr. Droop Richmond is the gentleman who, six years ago, wrote an elaborate paper to announce the discovery of a new element—of which nothing has since been heard,—he is certainly a high authority upon the new gases. But he has evidently not cured himself of the precipitancy of judgment he then displayed, otherwise he would not have committed himself to the groundless and utterly erroneous assumption that I had to wait for Rayleigh and Ramsay to learn about the classical experiment of Cavendish. I was acquainted with that before I left school.

It is satisfactory to find that this eminent authority does not upset or even seriously assail a single proposition advanced in the letter you did me the honour to publish. On the contrary, he concedes my main contention when he says that I "might wait a year or so, and give Professor Ramsay time to do the work he has mapped out for himself." The whole point is, that he has not taken the time everyone was willing to give him, but has hastily announced results—some of which are already proved to be erroneous, and none of which have yet been made out with scientific precision. The Cavendish residue was declared to be argon; and argon, *pace* Mr. Richmond, was loudly and even angrily declared to be an element, notwithstanding the warnings of the judicious. That residue is now declared to contain argon, krypton, neon, and metargon; but not one of the four has been any better made out than the famous Masrium that Mr. Richmond wrote of. There is nothing to show for them except spectral lines, some of which were noted years ago by Liveing and Dewar, and some by Moissan and Deslandres. Not one of the four thought of claiming the discovery of a new element, though all suspected its existence. Their procedure contrasts sharply with that of Professor Ramsay.

I am happy to be able to agree with Mr. Richmond on one point—that the real discoverer of argon is Lord Rayleigh. What he felt "as a physicist" I do not know, but I shrewdly suspect that he felt as a man more than than he has told the public. Whatever he felt as a physicist, he did not "associate himself with a chemist." It was the other way about; the chemist compelled Lord Rayleigh to accept a wholly unsought association with him. Lord Rayleigh, as he has told us himself, was directed by Professor Dewar to the experiment of Cavendish as the solution of his difficulty about the discrepant weights of nitrogen from different sources. But for that fortunate circumstance he would have lost more than the half share of the fruit of his admirably solid and accurate work.

For the direction subsequently given to the work, Lord Rayleigh—as a physicist, and not a chemist—is responsible only indirectly and under compulsion.

I have the more pleasure in thus fully correcting my "inadvertence," which I regret, Sir, to see somewhat illogically charged against you, because Professor Ramsay, with his usual scrupulous fairness, has hastened to point out that both Lord Rayleigh and Mr. Travers have a large share in what has been done.—I am, &c.,

Suum Cuique.

London, June 27, 1898.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvi., No. 18, May 2, 1898.

Researches on the State in which Silicon and Chromium occur in Siderurgical Products.—A. Carnot and M. Goutal.—The authors have already found that silicon and chromium combine with iron, manganese, and carbon; but the complexity of these compounds has necessitated further researches, which are here described. They also observed the existence of other compounds of silicon besides the silicide of iron, and these are now given with greater accuracy. Amongst other things, they conclude, from a number of experiments, that these siderurgic products contain two combinations of iron and silicon corresponding to the formulæ SiFe and $SiFe_2$; further, when sufficiently rich in manganese they may contain a silicide of the form $SiMn_3$. In the case of ferrochromes, there should be three molecules of carbide of chromium with one molecule of carbide of iron.

Dimethylamido-diethylamido-orthobenzoyl and Orthobenzylbenzoic acids, and some of their Derivatives.—A. Haller and A. Guyot.—The authors state that the memoir recently published by M. Limpricht (*Liebig's Annalen*, ccc., p. 228) contains results already published by them (*Comptes Rendus*, cix.; *Ber. der Deut. Chem. Ges.*, xxviii.; *Bull. Soc. Chim.*, [3], vols. xv. and xvii., &c.), as well as other results since obtained. The paper is partly controversial, but a number of new compounds are described.

On the Radiations emitted by Thorium and its Compounds.—G. C. Schmidt.—The author points out that the paper recently read at the Academy by Mdlle. Curie on this subject was anticipated by his communication to the Physical Society of Berlin on Feb. 4, 1898. He now gives the values he obtained with citrate of uranium, nitrate of uranium, oxide of thorium, sulphate of thorium, and nitrate of thorium.

On Iodide of Glucinum.—P. Lebeau.—Already inserted in full.

New Reaction of Tertiary Alcohols and their Ethers.—G. Denigès.—To apply the method already described by the author (*Comptes Rendus*, cxxvi., p. 1145) to the tertiary alcohols, it is necessary to heat a few c.c. of the alcohol in question with a few c.c. of the mercuric reagent used for the ethenic carbides, viz., HgO, 50 grms.; H_2SO_4, 200 grms.; and water, 1000 grms. A more or less yellow precipitate is at once formed; it sometimes has a reddish tinge, varying according to the alcohol used. The present paper is confined principally to the best known ones, and those easiest to obtain; that is, trimethyl carbinol, and ethyl dimethyl carbinol, so as to show the identity of the derivatives obtained with these alcohols and the corresponding ethenic carbides. The ethers of the tertiary alcohols also react with mercuric sulphate when gently warmed, furnishing yellow mercuric compounds. The action is very distinct with the tertiary nitrite of amyl used in medicine.

Action of Alkalis on Ouabaine.—M. Arnaud.—The alkalis do not hydrolyse ouabaine even when boiled, but give rise to a dehydrated derivative formed without splitting up and without the production of reducing sugar. The body formed is a monobasic acid, which decomposes the alkaline carbonates or the alkaline earths, and reddens blue litmus. Ouabaic acid, as it is called, is a yellowish white amorphous body, resembling gum; it is very soluble in water, slightly so in alcohol, but insoluble in ether. It melts at about 235°, decomposing and giving off a gas smelling of caramel. Its formula, deduced from the analysis of its salts, is $C_{30}H_{48}O_{13}$. The author proceeds to describe a number of its compounds, such as the ouabates of sodium, strontium, barium, &c.

Action of Bromine in the presence of Bromide of Aluminium on some Phenols.—F. Bodroux.—The author has applied the method of MM. Blumlein and Flessa to the bromidation of a number of phenols of the benzenic series by treating the phenol with an excess of bromine containing 1 per cent of aluminium in solution. After six hours the mixture is evaporated and treated with an appropriate solvent. The results obtained from nine different phenols are described at length. The action of bromine on the nitrophenols was found to be less strong in the presence of bromide of aluminium than when this latter body was not present.

The Monophosphoric Ethers.—J. Cavalier.—A criticism on a note recently presented to the Academy by M. Belugou (*C. R.*, April 18, 1898). The authors do not agree on all points.

Berichte der Deutschen Chemischen Gesellschaft.
December 13, 1897.

Reciprocal Transformation of Optical Isomers one in the other.—P. Walden and O. Lutz.—The authors have noticed the remarkable fact that when a solution of ammonia in methylic alcohol is made to act on a solution of left-handed chlorosuccinic acid, or left-handed bromosuccinic acid in the same solvent, and the rotatory power be followed with the polarimeter, it will be seen that the deviation gradually becomes less and less, disappears, and then becomes levogyre. It remains constant at the end of ten or twelve hours.

Regularity of the Increase of the Boiling-points of the Isomers of the Fatty Series.—N. Menschutkin.—The variations of the boiling-points of the isomeric alcohols, and in general the saturated compounds of the fatty series, depend—(1) On the length of the principal hydrocarbon chain; (2) on the number of lateral chains and their manner of attachment to the principal chain; (3) on the distance of the point of attachment of these chains from the functional grouping. As examples, the amylic and hexylic alcohols are cited.

Contributions to the Study of the Hydrocarbon Chains of the Fatty Series.—N. Menschutkin.—The author has studied the speed of the reaction of the fatty amines with bromide of allyl at 100°, using the following proportions:—Amine, 2 mols.; bromide of allyl, 1 mol.; benzene, 15 parts. He finds that the value of K decreases rapidly when passing from a lower to a higher homologue if the atoms are simply attached and the chain remains open. Whatever the constitution of the amine, the speed of the reaction is always greater with bromide of methyl than with bromide of allyl. With an amine having a secondary chain, the speed of the reaction varies little when the longest of the hydrocarbon branches is lengthened.

Stereo-isomeric Chlorobromosuccinic Acids.—P. Walden.—A racemic chlorobromosuccinic acid was prepared by heating 10 grms. of chlorofumaric acid with 35 grms. of a solution of HBr gas in acetic acid first to 125° and then to 140° in a closed glass vessel. On cooling, the product crystallises out in plates; it decomposes at 235—237°. Distilled with an excess of P_2O_5 it is transformed into chloromalic anhydride, boiling at 205°.

Some Derivatives of Prozane.—J. Thiele and W. Osborne.—The authors give the name "prozane" to the hypothetical compound $NH_2.NH.NH_2$. By acting on nitrate of diazoguanidine with CNK, the cyanide $CN.N = N.NH.C\begin{smallmatrix}=NH_2\\ \diagdown NH\end{smallmatrix}$ is obtained in difficultly soluble yellow needles. Mineral acids transform it into formamido-diazo-amino-formamidine, crystallising also in yellow needles, and detonating at 140°. The careful reduction of the formamide gives the compound $NH_2.CO.NH.NH.NH.C\begin{smallmatrix}=NH\\ \diagdown NH_2\end{smallmatrix}$, which decomposes spontaneously at a low temperature.

Some Organo-metallic Derivatives.—A. Michaelis.—Several series of organo-metallic and organo-metalloidic compounds have been prepared by acting on certain aromatic compounds with the chlorides of selenium, tellurium, bismuth, &c.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Decolourising Oils.—Would any of your kind readers give me the names of materials used in decolourising oils, either with a hot or cold process, such oils to be used for lubricating purposes and to have no acid reaction when finished.—H. Matthews.

THE CHEMICAL NEWS.

Vol. LXXVIII., No. 2015.

THE ACTION OF DI-ISOCYANATES UPON AMIDO-COMPOUNDS.

By H. LLOYD SNAPE, D.Sc., Ph.D.

In a paper published in the Chemical News (lxxiii., p. 37) I described the behaviour of diphenylene di-isocyanate towards ammonia and aniline. I have since submitted the same cyanate to the action of phenyl-hydrazine. As far as I can discover, the reaction of phenyl-hydrazine upon a di-isocyanate has not been examined; but if the former acted similarly to ammonia and aniline, two molecules of the base would combine directly with one molecule of the di-cyanate.

$$\begin{array}{l} C_6H_4{\cdot}NCO \\ | \\ C_6H_4{\cdot}NCO \end{array} + 2C_6H_5{\cdot}NH{\cdot}NH_2 = $$

$$= \begin{array}{l} C_6H_4{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}C_6H_5 \\ | \\ C_6H_4{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}C_6H_5. \end{array}$$

Combination was actually found to occur in accordance with this equation.

Diphenylene di-Phenylsemicarbazide.

Diphenylene di-isocyanate was dissolved in absolute ether and mixed with an ethereal solution of phenyl-hydrazine, the latter being taken in excess of the quantity theoretically required. A white powder immediately separated. This was extracted with boiling alcohol. The residue did not melt at 300°, and was insoluble in ether, chloroform, carbon tetrachloride, benzene, and petroleum-ether. As no suitable solvent was discovered for this compound, it was at once analysed, after drying *in vacuo* over sulphuric acid, and was found to have the constitution anticipated.

0·1899 gave 0·4816 CO_2 and 0·0953 H_2O. C = 69·16; H = 5·57.
0·0999 gave 16 c.c. moist N at 17° and 773·7 m.m. N = 18·87.
Required for $C_{26}H_{24}N_6O_2$, C = 69·03; H = 5·31; N = 18·58 per cent.

On the addition of a solution of copper sulphate to an alcoholic solution of the above substance a chocolate-brown colouration was obtained, which changed to green on the addition of ammonia.

1-2-4 *Toluylene di-Phenylsemicarbazide*, $CH_3{\cdot}C_6H_3(NH{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}C_6H_5)_2$.

This compound was produced by a precisely similar reaction, substituting the toluylene for the diphenylene di-isocyanate. The product was in this case, however, difficultly soluble in alcohol, and was re-crystallised from the solvent. The crystals thus obtained decomposed, and rose in a capillary tube at 203°. They were insoluble in ether, chloroform, benzene, petroleum ether, and carbon disulphide. A few drops of copper sulphate solution, when added to an alcoholic solution of the substance, gave a wine-red colouration, which changed to green on the addition of ammonia.

0·204 gave 0·4803 CO_2 and 0·1066 H_2O. C = 64·21; H = 5·80.
0·1228 gave 21·9 c.c. moist N at 14° and 776·9 m.m. N = 21·45.
Required for $C_{21}H_{22}N_6O_2$, C = 64·62; H = 5·64; N = 21·54 per cent.

1-2-4 *Diphenyl-toluylene-diurea*, $CH_3{\cdot}C_6H_3(NH{\cdot}CO{\cdot}NH{\cdot}C_6H_5)_2$.

When an ethereal solution of toluylene di-isocyanate was added to aniline also dissolved in absolute ether, combination took place immediately, and was attended by evolution of heat. By re-crystallisation from alcohol, microscopic needles were obtained which melted at 261° with accompanying decomposition, a gas being evolved which had the odour of phenyl cyanate. The crystals were only slightly soluble in methyl, ethyl, and amyl alcohol, and were insoluble in ether, chloroform, carbon tetrachloride, benzene, toluene, petroleum ether, and carbon disulphide, but dissolved readily in concentrated sulphuric acid.

0·1936 gave 0·4963 CO_2 and 0·0999 H_2O. C = 69·91; H = 5·73.
0·2231 gave 0·5732 CO_2 and 0·1132 H_2O. C = 70·07; H = 5·64.
0·1939 gave 25·9 c.c. moist N at 19° and 767·8 m.m. N = 15·51.
Required for $C_{21}H_{20}N_4O_2$, C = 70·00; H = 5·56; N = 15·55 per cent.

Kuehn described (*Berichte d. D. Chem. Gesell.*, xviii., 1477) a compound having the above formula, which he obtained by the action of phenyl isocyanate upon meta-toluylene-diamine. It was to be anticipated that this would be identical with the compound prepared as above. He states, however, that the substance was insoluble in all ordinary solvents save aniline, by which it was decomposed, and that its melting-point was above 300°. On repeating Kuehn's experiment, a fine white amorphous powder was obtained, which did not melt even at 325°; bnt, after boiling with alcohol, the residue and also the crystals from the alcoholic solution melted at 261° with decomposition, and appeared to be in every respect identical with that obtained from the toluylene di-cyanate. The compound of higher melting-point (as prepared by Kuehn's method) was also successively extracted with ether, chloroform, petroleum ether, benzene, and carbon disulphide. A very small quantity was dissolved out by the first two solvents named, and again the residue melted at about 260°.

1-2-4 *Toluylene di-urea*, $CH_3{\cdot}C_6H_3(NH{\cdot}CO{\cdot}NH_2)_2$.

A stream of dry ammonia gas was led into a solution of meta-toluylene di-isocyanate in absolute ether. The white precipitate yielded, by crystallisation from water, tufts of minute crystals which melted and rose in a capillary tube at ca. 252°. The crystals were only sparingly soluble in alcohol, and were insoluble in ether, chloroform, benzene, petroleum-ether, and carbon disulphide.

0·1856 gave 41·6 c.c. moist N at 14·3° and 775·5 m.m. N = 26·87.
Required for $C_9H_{12}N_4O_2$, N = 26·92 per cent.

Strauss described (*Liebig's Annalen*, cxlviii., 159) a substance which he named toluylene di-urea. This he obtained by the action of potassium cyanate upon the sulphate of a base which he terms "toluylen-diamin." The only such compound then known was the 1-2-4 isomeride; and hence it was to be anticipated that the urea obtained by him would be identical with that described above. He stated that the melting-point of the substance prepared by him was 220°. As the melting-point was about 30° lower than that obtained by me, I repeated Strauss's experiment. The sulphate was prepared from the same sample of meta-toluylene-diamine (m.pt. 99°, b.pt. 282—283°, obtained from Kahlbaum) as that I had used in the preparation of the di-isocyanate. The product, which separated on standing, was re-crystallised first from water and then from alcohol. The crystals thus obtained melted with decomposition at ca. 252°, and that they consisted of the di-urea was shown by the following analytical results:—

0·195 gave 0·3689 CO_2 and 0·1025 H_2O. C=51·59; H=5·84.
0·1006 gave 22·5 c.c. moist N at 10° and 763 m.m. N=26·88.
Required for $C_9H_{12}N_4O_2$, C = 51·92; H = 5·77; N = 26·92 per cent.

Lussy records (*Berichte d. D. Chem. Gesell.*, viii., 291) that he obtained the same substance as that prepared by Strauss, by the action of ammonia on toluylene di-isocyanate. The only difference between Lussy's experiment and my own, as far as may be determined from the literature, is that he prepared his di-isocyanate by the action of phosphoric anhydride upon the corresponding urethane, whereas I obtained mine direct from the toluylene diamine by the action of phosgene, by the method described by me (*Journ. Chem. Soc.*, xlix., 255). As, however, the melting-points of both the cyanate and the urethane prepared by Lussy and myself are in agreement, this does not account for the large difference in the melting-points of the di-urea.

University College of Wales, Aberystwith.

SEPARATIONS WITH ALKALINE CHROMATES.

By HARRY BREARLEY.

Those reactions which, by the formation of basic chromates, interfere with the separation of aluminium, iron, manganese, chromium, &c., from chromic acid, may be made the basis of a number of useful separations. It is possible, also, to use the chromates to suggest an explanation, by analogy, of some obscure points in the basic acetate separation of iron.

The Separation of Iron and Aluminium.

Two or three times during the past year there has been occasion to notice, when an acetate separation of iron was made in the presence of aluminium and an alkaline chromate, that a considerable portion of alumina was to be found in the filtrate. A comparison of the behaviour of ferric and aluminic solutions on adding K_2CrO_4 clearly explains the result; for while ferric salts are precipitated more readily in hot than in cold solutions, the aluminic salts are precipitated less readily in the hot solution, and moreover the latter, in any case, less readily forms basic chromates than the former.

Turning to "neutralised" solutions,—that is, those holding the full amount of dissolved hydrate,—we find that half a grm. of iron may be readily precipitated by 10 c.c. potassium chromate (12½ grs. per litre), but that half a grm. of Al in a like state needs 50 c.c. K_2CrO_4 to form a partial precipitate. More strikingly still, the ferric precipitate is insoluble, in hot solution, in presence of free acetic acid, while the Al precipitate is *very* easily soluble, so that, although half a grm. of iron is precipitated as before with 10 c.c. K_2CrO_4 when 10 c.c. of acetic acid (33 per cent) is present, half a grm. of Al with its 50 c.c. K_2CrO_4 does not show the faintest trace of a precipitate when the same amount of acetic acid is present.

The obvious inference is that one has only to neutralise the mixture (Al+Fe), heat to boiling, add potassium chromate, and straightway effect an easy separation of iron and aluminium. Unfortunately such an inference may not be supported experimentally. The difficulty consists of the iron refusing to be precipitated until many times more K_2CrO_4 has been added than would be needed if no aluminium was present, and in ultimately carrying down with it so great a proportion of Al as spoils a quantitative separation.

A set of circumstances almost parallel can be associated with the behaviour of a "neutralised" mixture of Fe and Al salts to alkaline acetates. This latter case, however, is of such frequent occurrence in the steel works laboratory that one has ceased altogether to be astonished at it. Even the text-books special to steel analysis, after drawing attention to the solubility of the hydrates and acetates of alumina in free acetic acid, explain the absence of this element from the filtrates by the not too satisfactory remark that "the chromium and aluminium are completely carried down with the iron precipitate."

Inured as one may be to the above phenomenon of acetate separations, the behaviour of the mixed solutions of Fe and Al to an alkaline chromate has all the novelty of a most unexpected result, and one is prompted by disappointment to question the right of solutions to behave so.

The cause of the failure with chromate may go some way towards explaining the failure with acetate, and the liberty of chronicling a failure may be further justified by some peculiarities which were brought to light in attempting to find experimentally the cause of failure.

Soda carbonate had been used for "neutralising" the metallic solutions. This would precipitate the iron as hydrate and the alumina as basic carbonate; for the sake of brevity, however, we may speak of the united precipitates as hydrates.

Solubility of Ferric Hydrate and Basic Al Carbonate in Ferric Chloride and Aluminic Chloride.

According to "Comey's Dictionary," p. 6, precipitated aluminium hydroxide is insoluble in ferric chloride. Gmelin ("Handbook," v., 277) states the contrary to be the case. I find that 1/10th of a grm. of iron as ferric chloride readily dissolves a quarter of a grm. of Al which has been freshly precipitated from a solution of Al_2Cl_6, by adding an equivalent amount of soda carbonate. The solution becomes dark mahogany-coloured, just as when ferric hydrate is being dissolved. In 1/10th of a grm. of Al, in a similar way, one may dissolve precipitated ferric hydrate, but here the reaction is much slower; however, more than a quarter of a grm. is dissolved with only a faint opalescence; and when half a grm. of iron, as ferric hydrate, is added, only a very small precipitate remains undissolved on standing.

A mixture of ferric and aluminic chloride, on being neutralised, offers every advantage for this mutual solubility to display itself. This being done, the added chromate might be assumed to precipitate the remnant of ferric chloride along with the dissolved ferric and aluminic hydrates. This would account for so much of the Al being carried down with the iron. If we assume that the chloride of aluminium, having dissolved large amounts of $Fe_2(HO)_6$, must be itself decomposed before the iron can be completely separated, and so account for the larger amounts of K_2CrO_4 found to be necessary, we are unable to account for so much of the alumina as does always exist in the filtrate. I am inclined to think that the solution of ferric hydrate in the Al_2Cl_6 does not take place, owing to the comparative slowness of the reaction, to any great extent; and for the rest I think it is more satisfactory, and not more difficult, to assume that the properties of the ferric chloride are greatly modified by the dissolved basic carbonate of alumina which it has dissolved, one result of which is that it behaves to the K_2CrO_4 rather as an aluminic than a ferric salt.*

The following experiments indicate a reaction between the neutralised solutions of Al and Fe, whose significance in this connection can be well understood, but whose nature has not yet been made out. In each test ½ grm. Fe and ¼ grm. Al was used, volume of solution about 300 c.c.:—

(1) Solution completely neutralised: added 20 c.c. K_2CrO_4, no precipitate; 10 c.c. K_2CrO_4 more, precipitate

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* If the ferric chloride, on "neutralisation," dissolved the combined precipitates in more than equivalent portions, and so preserved itself more as undecomposed chloride holding dissolved hydrates, it would necessarily need larger amounts of K_2CrO_4 to decompose it, but not nearly such large amounts as are found to be necessary.

on continued boiling; less than one-fourth of the Al was found in the filtrate.

(2) Repeated (1) and continued the boiling for some time; then added 10 c.c. of acetic acid, with intent to redissolve the precipitated $Al_2O_3,yCrO_3$, which is so easily soluble in acetic acid; but the total precipitate dissolved, although the ferric compound is quite insoluble alone. If the acetic acid be added before the chromate, it is necessary to add about 70 c.c. of the latter, and then the filtrate contains also considerable iron.

(3) Neutralised the Al_2Cl_6 and Fe_2Cl_6 separately in hot solutions, then cooled and mixed them in separate portions. A precipitate is formed, and this the more readily as the proportion of aluminium is greater. The precipitates were collected on a filter, and after the mother-liquor was removed they were washed with cold water. *They dissolved* to a clear dark reddish liquid. Hot water very readily dissolves the precipitates, and gives a perfectly clear solution, very much like a "neutralised" solution of ferric chloride.

(4) "Neutralised" the solutions separately as in (3), and together as in (1), in each case using the same amounts of soda carbonate. The latter remained clear on standing or heating, but on mixing the separately neutralised solutions a precipitate was formed. The filtrate was perfectly clear and colourless, and contained nearly the whole of the aluminium.*

(5) One-tenth of a grm. iron, as ferric chloride, in which is dissolved ¼ grm. Al precipitated from its chloride solution with soda carbonate. Raised to boiling; needs 40 c.c. of the K_2CrO_4 to form a precipitate.

The foregoing experiments show conclusively, I think, that no complete separation of iron and aluminium can be made on "neutralised" solutions. The very intimate association of the two metals, under such conditions, suggest that no such separation will ever be effected.

Separation of Iron and Aluminium in Normal Solutions.

When only the free acid of a solution of iron and aluminium salts has been neutralised (without forming dissolved hydrates) the foregoing considerations do not apply. Such a state may be attained with sufficient accuracy by noting the change from yellow to red which characterises the solution of ferric hydrate in its chloride.

If it were possible to precipitate the whole of the iron when it exists as ferric chloride, then our object might easily be attained, but unfortunately—even from pure ferric chloride solutions—the iron is not completely precipitated, nor does increasing the potassium chromate noticeably better the precipitation. And, again, the precipitate is somewhat soluble in the cold mother-liquor, so that filtrations must be preserved as hot as possible.

This separation was tested on a mixture of half a grm. each of iron and aluminium. The iron was precipitated as just explained with K_2CrO_4; the filtrate was evaporated and treated with caustic soda (from Na), the small quantity of iron filtered off, and the iron precipitated as phosphate.† The precipitate was washed until the washing showed no turbidity with silver nitrate. The aluminium recovered, calculated from the ignited $AlPO_4$, was 0·5030 grm., which is less than 1 per cent from the amount added.

Separation of Iron and Chromium.

This separation cannot be completely effected in "neutralised" solutions, for the reasons previously stated in connection with aluminium.

Separation of Iron and Nickel.

Generally potassium chromate would seem to be a most excellent reagent in the same office as alkaline acetates for separating iron from various elements. There is no occasion whatever to go back on the strong recommendation of the acetate separation of iron and nickel which has been previously made; at the same time it is desirable to acknowledge the service of a reagent which can be used in much larger excesses without fear of ill results, and moreover which can be used where the acetate separation of iron and nickel begins to break down, viz., in the presence of considerable amounts (10 per cent or more) of aluminium.

Nickel can form a number of basic chromates just as iron can, but the separate compounds behave very differently under simple and easily arranged circumstances. The iron compound is readily formed in heated solutions, and is practically insoluble in dilute solutions of acetic acid. On the other hand, the formation of the nickel compound is much less readily accelerated by heating, and is *very readily* soluble in dilute acetic acid. The process is based on these facts, but, as it differs from the usual acetate separation only in the substitution of a chromate for an acetate, it needs no further description.

One grm. of iron (neutralised solution) is abundantly precipitated by 10 c.c. K_2CrO_4 (12½ grs. per litre), and the behaviour of an excess of the precipitant on an accompanying 0·1 grm. of nickel is as follows:—

10	30	50	c.c. chromate added,
0·1000	0·0998	0·0918	grs. Ni recovered,

which are better separations than proportional excesses of acetate would give even in presence of 1 per cent acetic acid. When the chromate separations are made in a 1 per cent acetic acid solution, the range of accuracy is enormously increased. The following are examples, using the previous amounts of iron and nickel:—

30	50	70	c.c. chromate used.
0·1004	0·1000	0·1000	grs. nickel recovered.

The $Fe_2(HO)_6$ liberated by the decomposed ferric chloride can react with K_2CrO_4 to form basic chromates, and hence the larger excess of the precipitant there is, the less basic these chromates are, so that the colour of the filtrate is not proportional to the excess of K_2CrO_4 used. When ample chromate is added the filtrate may be hardly coloured. In some ways the presence of K_2CrO_4 in the filtrate may be an advantage. For instance, in the cyanometric estimation of the nickel it readily indicates the neutrality of the solution. Even highly coloured filtrates have not been found to be harmful.

In preparing for the cyanometric estimation of the separated nickel, it is necessary, in presence of chromic acid, to proceed in a certain order. First add the ammonium sulphate (for the purpose of heightening the AgI turbidity, &c.), and then make alkaline with ammonia. The reason for this is that the ammonia sulphate prevents the formation, in an alkaline solution, of a basic nickel chromate (a brown precipitate which might be mistaken for ferric hydroxide), which does not so readily combine with the cyanide. If the reverse order is followed, the added ammonia sulphate does not easily dissolve this precipitate.

The acetate separation of iron from nickel in presence of aluminium was incomplete, because a greatly increased amount of acetate was needed under these conditions. In a like manner, an increased amount of chromate is necessary, but the increase is quite covered by the latitude which can safely be allowed when using the latter reagent.

The nickel is accompanied by part of the aluminium. As our test analyses contained known amounts of nickel, we peformed the titration by adding a slight excess of cyanide, fractionally filtering off the alumina, and completing the reaction on the aliquot filtrate. Such results were always low. To make an accurate estimation it is necessary to keep the alumina in solution by adding (not a needlessly large amount) tartaric acid; or if the amount of Ni is approximately known, by adding a small excess of cyanide to the faintly acid or neutral solution, and

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* Judging from the bulk precipitated by ammonia when compared with a standard.

† This procedure completely effects the separation of the alumina from the chromic acid (Chem. News, lxxvii., 179),

then making alkaline, filtering off Al_2O_3, &c. This point will be more fully dealt with in a later paper on cyanometric estimations.

The Separation of Iron and Copper.

The most favourable separation of these elements with acetate were 1 or 2 per cent too low. The Schwarzenberg separation even, which is not easy to perform well, did not give quite accurate results. With chromate the separation is accurate with a wider range of the precipitant than the corresponding nickel separation is: thus 50 c.c. K_2CrO_4, used in the previous—non-acetic nickel-iron—separation, separated only 91·8 per cent of the added nickel; in a like copper separation 97·0 per cent was separated. Other results are:—

10	30	c.c. chromate used.
0·0998	0·1003	grs. Cu recovered.

The chromate compound of copper is also *very* soluble in dilute acetic acid, and a greatly increased range of accuracy may fairly be expected to attend its use in case any circumstance should require very large excesses to be used.

In January of this year, when the suitability of potassium chromate for the copper-iron separation was first suggested, our Mr. Jervis made a number of tests which fully illustrated the accuracy of the process. The separated copper may be easily estimated by the soda cyanide process (Chem. News, lxxvi., 189 and 291).

It is anticipated that other separations may be made. The accuracy of the preceding separations, and the wide differences under which it may be maintained, are points of some value where technical analyses are performed by operators not too skilled.

Totley, near Sheffield.

RECENT EXPERIMENTS ON CERTAIN OF THE CHEMICAL ELEMENTS IN RELATION TO HEAT.*

By Professor W. A. TILDEN, D.Sc. F.R.S.

The discovery that different substances have different capacities for heat is usually attributed to Irvine, but there can be no doubt that Black, Crawford, and others contributed to the establishment of the idea. The fact that equal weights of different substances, in cooling down through the same number of degrees, give out different amounts of heat, may be illustrated by the well-known experiment, in which a cake of wax is penetrated with different degrees of rapidity by balls of different metals heated to the same temperature. But, for the quantitative estimation of the amounts of heat thus taken up and given out again—that is, the *specific heats*—the physicist must resort to other forms of experiment, each of which presents difficulties of its own. Broadly speaking, three principal methods have been used in the past for this purpose. The first is based upon the observation of the exact change of temperature produced in a known mass of water, by mixing with it a known weight of the substance previously, at a definite temperature above or below that of the water. The second consists in determining the quantity of ice melted, when the heated body is brought into contact with it in such a way that no heat from any other source can reach the ice. And the third method consists in observing the rate at which the temperature of the heated body falls through a definite range of degrees, when suspended in a vacuous space, as compared with the rate of cooling of another body taken as the standard.

The process of intermixture with water was used by the earlier experimenters in the last century, and some of the best results extant have been obtained by this method, which, however, is not so easy as it appears when the highest degree of accuracy is desired.

Lavoisier and Laplace, in 1780, devised the ice calorimeter which bears their name; and in a most interesting memoir, which is reprinted among Lavoisier's works, they show that they were familiar with the idea which in modern times is expressed as the principle of the conservation of energy. In this memoir they give the results of experiments, in which the specific heats of iron, mercury, and a few other substances are estimated with a very tolerable approach to accuracy. Although many of the metals were known to them, and supposing they had persisted in this work, it would not have been possible for them to make the discovery which was reserved for Dulong and Petit thirty-five years later, for the atomic theory had not then been conceived, and no elemental combining proportions had been determined.

Dulong and Petit* seem to have used at first the method of mixtures, and to have found, by direct experiment, that the specific heat of solids (metals and glass) increases with the temperature. They also studied (after Leslie) the laws of cooling of bodies; and two years after the publication of their first paper on the subject, they (Petit and Dulong, *sic*) arrived at the remarkable general expression which is associated with their names.†

After pointing out that all the results of previous experiments except those of Lavoisier and Laplace are extremely incorrect, they describe their own conclusions obtained by the method of cooling, conducted with many precautions to avoid error. The numerical expression of their experimental results is given in the following table:—

Copy of Table by Petit and Dulong.
(*Ann. Chim. Phys.*, 1819, x. 403.)

	Specific heats.	Atomic weights (0=1).	Atomic weight × specific heat.
Bismuth	0·0288	13·30	0·3830
Lead	0·0293	12·95	0·3794
Gold	0·0298	12·43	0·3704
Platinum	0·0314	11·16	0·3740
Tin	0·0514	7·35	0·3779
Silver	0·0557	6·75	0·3759
Zinc	0·0927	4·03	0·3763
Tellurium ..	0·0912	4·03	0·3675
Copper	0·0949	3·957	0·3755
Nickel	0·1035	3·69	0·3819
Iron	0·1100	3·392	0·3731
Cobalt	0·1498	2·46	0·3685
Sulphur	0·1880	2·011	0·3780

The statement of the relation indicated in the last column of figures is expresseed in the following words of the author, page 405: "Les atomes de tous les corps simples ont exactement la même capacité pour la chaleur."

Here the question rested, till resumed many years later (1840) by Regnault, who in his first memoir‡ pointed out the difficulties which attend the acceptance of the statement of Petit and Dulong in the form in which they gave it. He then discussed the three principal experimental methods, viz.: (1) fusion of ice; (2) mixture with water or other liquid; and (3) cooling; and decided in favour of the second, which he used throughout his researches. The general form of the apparatus used by the great physicist has been a model for the guidance of successive experimentalists since his time.

Another quarter of a century elapsed before the question of the specific heats of the elements was resumed by Hermann Kopp. His results were communicated to the Royal Society, and are embodied in a paper printed in the *Philosophical Transactions* for 1865. After reviewing the

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* A Lecture delivered at the Royal Institution of Great Britain, Friday, May 13th, 1898.

* *Ann. Chim.*, 1817, vii., 144. † *Ibid.*, 1819, x., 395. ‡ *Ibid.*, 73, 5.

work of his predecessors, he described a process by which he had made a large number of estimations of specific heat, not only of elements, but of compounds of all kinds in the solid state. Concerning his own process, however, he remarks that "the method, as I have used it, has by no means the accuracy of that of Regnault" (p. 84).

In 1870 Bunsen introduced his well-known ice-calorimeter. This is an instrument in which the amount of ice melted by the heated body is not measured by collecting and weighing the water formed, but by observing the contraction consequent upon the change of state. The results obtained by Bunsen himself are uniformly slightly lower than those of Regnault for the same elements.

Since that time, experiments have been made by Weber, Dewar, Humpidge, and others, in connection especially with the influence of temperature in particular cases.

Setting aside the elements, carbon, boron, silicon, and beryllium, as providing an entirely separate problem, the question is whether the law of Dulong and Petit is strictly valid when applied to the metals. Kopp, in the discussion of his subject, came to the conclusion that it is not; but the grounds for this conclusion are unsatisfactory, since neither the atomic weights nor the specific heats were at that time known with sufficient accuracy. It has been customary to assume that the divergences from the constant value of the product, At. Wt. × Sp. Ht., are due partly to the fact that at the temperature at which specific heats are usually determined, the different elements stand in very different relations to their point of fusion; thus, lead at the temperature of boiling water is much nearer to its melting point than iron under the same conditions. The divergences have also been attributed to temporary or allotropic conditions of the elements. As to the relation to melting point, the specific heats of atomic weights seem to be practically the same in separate metals and alloys of the same which melt at far lower temperatures. For example, the atomic heat of cadmium is 6·35; of bismuth 6·47; of tin, 6·63; and of lead, 6·50; while the mean atomic heat in alloys of bismuth with tin and lead with tin ranges from 6·40 to 6·66 (Regnault), which is practically the same. Again, while the melting point of platinum is at a white heat, the metal becomes plastic at a low red heat, and yet the specific heat at this lower temperature is very little less than it is near the melting point. The properties of many other metals, notably zinc and copper, change considerably at temperatures far removed from their melting points without substantial change in their capacity for heat.

As to allotropy, it is a phenomenon which is comparatively rare among metals, and in the marked cases in which it occurs we have no information as to the value of the specific heats in the several varieties, such as the two forms of antimony and the silver-zinc alloy of Heycock and Neville, and they may be left out of account. Bunsen compared the so-called allotropic tin, obtained by exposing the metal to cold for a long time, and found it 0·0545 against 0·0559 for the ordinary kind (*Pogg. Ann.*, 141, 27). In dimorphous substances there is often no difference. Regnault found for arragonite 0·2086 and for calcite 0·2085 respectively. The differences between metals hammered and annealed, hard and soft, were also found by Regnault to be very small (*Ann. Chim.*, [3], ix.).

Hard steel ..	0·1175	Same, softened ..	0·1165
Hard bronze..	0·0858	Same, softened ..	0·0862

Kopp came to the conclusion, *first*, that each element in the solid state, and at a sufficient distance from its melting point, has *one* specific or atomic heat, which varies only slightly with physical conditions; and *secondly*, that each element has essentially the same specific or atomic heat in compounds as it has in the free state. This last is practically identical with the statement which is known as Neumann's law. With Kopp's conclusion I agree, but, from some of Regnault's results coupled with my own, the effect of *small* quantities of carbon and perhaps of sulphur upon the specific heats of metals is greater than has been supposed. If we take the results of Regnault and of Kopp and combine them with the most accurately known atomic weights, the products are still not constant.

Atomic Weights most accurately known (1897)
combined with Specific Heats.

	A.W. (H=1)	S.H. Regnault.	S.H. Kopp.	At. Ht. Regnault.	At. Ht. Kopp.
Copper	63·12	0·09515	0·0930	6·01	5·87
Gold	195·74	0·03244	—	6·35	—
Iron	55·60	0·11379	0·1120	6·33	6·23
Lead	205·36	0·03140	0·0315	6·45	6·47
Mercury liq. ..	198·49	0·03332	—	6·61	—
Mercury −78° to +10° sol... ..	198·49	0·03192	—	6·34	—
Silver	107·11	0·05701	0·0560	6·11	6·00
Iodine	125·89	0·05412	—	6·81	—

The "Law" of Dulong and Petit is therefore only an approximation; but this may perhaps be due to inaccuracy in the estimation of the specific heat, owing to impurity in the material used. That is the problem which I have endeavoured to solve.

The introduction by Prof. J. Joly of a new method of calorimetry, which depends upon the condensation of steam upon the cold body, and the excellent results obtained by the author in the use of the differential form of his instrument (*Proc. R. S.*, xlvii., 241), led me to think that with due attention to various precautions—such as exact observations of the temperatures, and practice in determining the moment at which the increase of weight due to condensation is completed—results of considerable accuracy might be obtained.

The problem is to find two elements, very closely similar in density and melting-point, which can be obtained in a state of purity, and then to determine with the utmost possible accuracy the specific heat of each under the same conditions.

The two metals cobalt and nickel were selected for the purpose. They were examined by Regnault, but the metals he used were very impure.

The cobalt employed in my experiments was prepared by myself. For the nickel I am indebted to Dr. Ludwig Mond. Both were undoubtedly much more nearly pure than any metal available in Regnault's time. The results obtained are as follows:—

Specific Heats of Cobalt and Nickel.
Pure fused.

	Cobalt, S. G. 21°/4°, 8·718.	Nickel, S. G. 21°/4°, 8·790.	
	0·10310		
	0·10378		
	0·10310	0·10953	too high ?
	0·10355	0·10910	
	0·10373	0·10930	
	0·10362		
Arith. mean ..	0·10348	0·10931	

The value arrived at for cobalt is much lower than that (0·1067) derived from Regnault's experiments, while that for nickel is practically identical with Regnault's, which is 0·1092. This is certainly too high.

Further experiments will be made, because a single well-established case of this kind is sufficient to decide the question. Already, however, I feel certain that Kopp's conclusion is right, and that the law of Dulong and Petit, even for the metals, is an approximation only, and cannot be properly expressed in the words of the discoverers. For, although the exact values of the atomic weights of these two elements, cobalt and nickel, are not known, it is certain that they are not so far apart as would be implied by these values for the specific heats.

Two other examples of somewhat similar kind are shown by gold and platinum, copper and iron.

For the gold I naturally applied to my colleague, Prof. Roberts-Austen. The platinum I prepared from ordinary foil, by re-solution and re-precipitation as ammonio-chloride, and subsequent heating. Both metals were fused into buttons before use. The atomic heats come closer together than those of Co and Ni.

Copper and iron differ considerably in melting-point, but both at the temperature of 100° are far removed from even incipient fusion. The copper was prepared from pure sulphate by electrolysis, the iron by reduction of pure oxide in pure hydrogen. Notwithstanding all our care, it was disappointing to find it contained 0·01 per cent of carbon, the source of which I am at a loss to explain. This iron is purer than any examined by Regnault or Kopp.

Specific Heats of Gold and Platinum.

Pure fused.

Gold, S. G. 18°/18°, 19·227.		Platinum, S. G. 18°/18°, 21·323.	
0·03052		0·03147	
0·03017		0·03150	
0·03035		0·03144	
Arith. mean ..	0·03035	Arith. mean ..	0·03147
Atomic heat ..	5·94	Atomic heat ..	6·05

Specific Heats of Copper and Iron.

Fused.

Copper (pure) S. G. 20°/20°, 8·522		Iron, S. G. 15°/15°, 7·745, contains 0·01 p.c. copper.	
0·09248		0·11022	
0·09241		0·11037	
0·09205			
0·09234			
Arith. mean ..	0·09232	Arith. mean ..	0·011030
Atomic heat ..	5·83	Atomic heat ..	6·13

The differences observed between cobalt and nickel, and between gold and platinum, are manifestly not due to allotropes or to differences of melting point, which in these cases can have no effect on the result. So large a difference must be due to peculiarities inherent in the atoms themselves; and differences of atomic heat are to a certain extent comparable with the differences observed in other physical properties, which, like specific volume, specific refraction, &c., are approximately additive.

If we try to think what is going on in the interior of a mass of solid when it is heated, the work done is expended not only in setting the atoms into that kind of vibration which corresponds to rise of temperature, that is, it makes them hotter, but partly in separating the molecules or physical units from one another (=expansion) and partly in doing *internal* work of some kind, the nature of which is not known. A difference between metals and non-metals has been brought out by the researches of Heycock and Neville, who find that metals dissolved in metals are generally monatomic; whereas it is generally admitted that iodine, sulphur, and phosphorus in solution are polyatomic. It is moreover remarkable that, although in respect to specific heat each element in a solid seems to be independent of the other elements with which it is associated, when the elementary substances are vapourised some rise in separate atoms like mercury, some in groups of atoms like iodine, sulphur, arsenic, and phosphorus, and as the temperature is raised these groups are simplified with very varying degrees of readiness.

The two metals, cobalt and nickel, with which I began my inquiry, have very nearly the same atomic weight, the value, 58·24 for nickel and that for cobalt 58·49, being calculated by F. W. Clarke from the results of a great many analyses by many different chemists. They are so close together that for a long time they were regarded as identical, and Mendeléef does not hesitate even to invert the order by making Co = 58·5 and Ni = 59. These metals, nevertheless, differ from each other in several very important chemical characters. Nickel, for example, forms the well known and highly remarkable compound with carbonic oxide discovered by Dr. Mond. Cobalt, on the other hand, produces many ammino-compounds to which there is nothing corresponding among the compounds of nickel.

Having put aside the common excuses for the observed divergences from the constant of Dulong and Petit, we are compelled to look round for some other hypothesis to explain them.

The constitution of carbon compounds is now accounted for by a hypothesis concerning the configuration of the carbon atom introduced by van 't Hoff and Le Bel twenty-five years ago, and which is now accepted by the whole chemical world. It seems not unreasonable to apply a similar idea to the explanation of those cases of isomerism which have been observed in certain compounds of the metals, notably chromium, cobalt, and platinum. This has already been done by Professor Werner, of Zürich. If the constitution of compounds can be safely explained by such hypothesis, this implies the assumption of peculiarities in the configuration of the individual constituent metals around which the various radicles are grouped in such compounds; and hence peculiarities in the behaviour of such metals in the elemental form may possibly be accounted for. For the atom of cobalt Professor Werner employs the figure of the regular octahedron. For nickel, therefore, which differs from cobalt in many ways, a different figure must be chosen. This, however, is for the present a matter of pure speculation.

THE ESTIMATION OF SUCCINIC ACID IN THE PRESENCE OF TARTARIC AND LACTIC ACIDS.

By MM. BORDAS, JOULIN, and DE RACZKOWSKI.

When we add a concentrated solution of nitrate of silver to a solution containing these three acids in the state of soluble neutral salts, the succinic acid is precipitated integrally, the tartaric acid partially, while the lactic acid remains in solution on account of the different solubilities of these three salts of silver.

This being admitted, the following is the manner in which we effect the estimation:—

The solution containing the three acids is exactly neutralised by means of a decinormal solution of potash. We note the number of cubic centimetres necessary, we then add an excess of a concentrated solution of nitrate of silver. The precipitate is filtered and washed until a drop of the filtrate is no longer precipitated by neutral chromate of potassium. Under these conditions the succinate of silver *only* remains on the filter, the tartrate of silver being completely dissolved by the wash waters.

The washed precipitate is transferred to a flask by means of a fine jet of water from the wash bottle, and two drops of a neutral solution of chromate of potassium are added; this decomposes the succinate of silver in suspension and forms chromate of silver. We then add such a quantity of a decinormal solution of sodic chloride that the precipitate becomes white and the liquid takes a yellow tint. It suffices then to pour in a solution of nitrate of silver, also decinormal, until the liquid commences to take a reddish-brown colour.

By subtracting the number of cubic centimetres of nitrate of silver from that of the decinormal chloride of sodium, we obtain the volume of the decinormal solution of nitrate of silver necessary to precipitate the amount of succinic acid present. 1 c.c. of this solution corresponds to 0·0059 of succinic acid. As, on the other hand, it is an easy matter to estimate the tartaric acid, the lactic acid can be obtained by difference.—*Journ. de Pharm. et de Chim.*, Series 6, vol. vii., No. 9.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 16th, 1898.

Professor Dewar, F.R.S., President, in the Chair.

(Concluded from p. 9).

*93. "*Reversible Zymohydrolysis.*" By Arthur Croft Hill, B.A.

This investigation was undertaken to ascertain whether zymohydrolysis is a reversible process or not. The hydrolysis of maltose by maltase was selected for the purpose, the enzyme being obtained by extracting dry and finely powdered low-fermentation yeast, which had been heated under certain precautions, as detailed in the paper. It was found that the extract could be sterilised without destruction of its activity by filtration through a Pasteur-Chamberland filter.

The analytical methods for estimating the extent of hydrolysis were (1) determination of the cupric-reducing power of the mixed sugars; (2) determination of the specific rotatory power. The details of the methods and limits of accuracy are dealt with fully in the paper. To simplify calculations, maltose is reckoned as maltose hydrate, $C_{12}H_{22}O_{11},H_2O$.

The zymohydrolysis of maltose into glucose is hindered by the presence of glucose and is incomplete, and both these effects are more marked the more concentrated the solution of sugar. The retardation is shown by two sets of experiments. In the first set, the initial velocities of conversion are compared in a solution of maltose of a certain concentration with that in a solution of half maltose and half glucose of like total concentration. The ratio of these velocities should be not greater than 2, if the glucose were without influence; actually it is much greater, being about 3 for a 4 per cent, and 4·85 for a 20 per cent sugar concentration. In the second set, the time curves are compared for two flasks, each containing initially the same concentration of maltose, while to one glucose has been added in equal concentration. If glucose were without influence, the time curve of conversion of maltose into glucose should be identical for each flask, but a much slower conversion occurs in that containing the added glucose, and the effect is much more marked with a total sugar concentration of 20 per cent than with one of 4 per cent.

When the enzyme acts in a 20 per cent solution of glucose, a small reverse action can be detected by the polarimeter. With a 40 per cent concentration, the reverse action is well marked, and when sufficient time has been allowed for this action, which is a slow one, to approach completion, the reversion indicated by the change in rotatory and cupric-reducing powers amounts to 15 per cent of the sugar. Control flasks show no change. With a 40 per cent solution of sugar, of which 75 per cent was glucose and 25 per cent maltose (hydrate), hydrolysis proceeded till 83·25 per cent of the total sugar was glucose, and the equilibrium point, therefore, for this concentration is not far from 84 parts glucose to 16 parts maltose (hydrate). Equilibrium points for various concentrations have been determined; and it is found that in dilute (2 per cent) solutions hydrolysis is practically complete. The same equilibrium point is approached either with a solution of maltose or with one of glucose of the same concentration.

Maltose has been detected as a product of the reverse action by the use of phenylhydrazine. An osazone having a greater solubility in boiling water than glucosazone has been separated, and this crystallises in plates, has the same percentage of carbon and nitrogen as maltosazone, but melts at a temperature somewhat lower than maltosazone from pure maltose, though not lower than that prepared from ordinary maltose under similar conditions, viz., from a mixture of maltose with excess of glucose to which some boiled enzyme solution has been added, the proteid being then removed as completely as possible before treatment with phenylhydrazine. The synthesised maltose has not yet been isolated, but it is considered that the evidence of its presence, coupled with the increase of optical rotatory power, and corresponding decrease in cupric-reducing power observed in concentrated glucose solutions in the presence of maltase, justify the conclusion that the zymohydrolysis of maltose is a reversible process.

Discussion.

Dr. Horace Brown congratulated the author on the important results he had obtained, and stated that, although some such reversed action was recognised when dextrose is acted on by dilute acids, this was the first time that anything of the kind had been shown to occur during prolonged enzyme action. He had been privileged to see the details of the author's work whilst it was in progress, and was quite satisfied that a reversal had really taken place. The alteration in optical and reducing properties, and the appearance of the osazone pointed strongly to the reversed product being ordinary maltose, but until this was isolated, and such isolation ought not to present any insuperable difficulties, he did not feel quite satisfied as to its nature. It could not be identical, however, with the isomaltose obtained by Emil Fisher by the action of acid on dextrose.

Mr. Ling thought that additional evidence was necessary before it could be definitely concluded that maltose was produced from glucose, and, as a possible means of deciding the question, suggested converting the product into acetyl derivatives instead of into osazones. Octacetylmaltose was a well characterised compound, and could, he thought, be separated from the acetyl derivatives of glucose.

94. "*The Solubility of Isomeric Substances.*" By James Walker, PhD., D.Sc., and John K. Wood, B.Sc.

In continuation of a research by Carnelley and Thomson (*Trans.*, 1888, 53, 782), the authors have investigated the solubility of the hydroxybenzoic acids, and the isomeric ureas, $C_7H_8N{\cdot}CO{\cdot}NH_2$, in various solvents.

The values obtained for the solubility of salicylic acid at different temperatures are one-third less than the values given by Bourgoin. The variation of the solubility of the hydroxybenzoic acids in water with the temperature is expressible up to 50° by a formula of the type proposed by Nordenskjöld, the equations being, for the ortho-acid, $\log S = 0{\cdot}01556t - 1{\cdot}0458$; for the meta-acid, $\log S = 0{\cdot}01793t - 0{\cdot}4188$; and for the para-acid, $\log S = 0{\cdot}0227t - 0{\cdot}7972$. With benzene as solvent, a formula of this type does not express the variation of the solubility with the temperature.

Congo red was found to be the best acidimetric indicator for salicylic acid and its isomerides.

The rule that the order of fusibility of isomeric substances is also the order of their solubility does not hold good for the hydroxybenzoic acids, but it is in general applicable to benzyl urea and its isomerides.

The rule that the order of solubility of isomerides is independent of the solvent is not strictly applicable in either of the cases investigated. The constancy of the solubility ratio observed by Carnelley and Thomson for para- and meta-nitraniline is not found either with the acids or with the ureas. The solubility ratios of the hydroxybenzoic acids in the same solvent vary considerably with the temperature.

95. "*Note on Nitration and Substitution in Nitro-compounds.*" By Arthur Lapworth, D.Sc., and Charles Mills.

It is known that (1) nitro-compounds yield chiefly meta-derivatives with most substituting agents, but orthonitrophenols when acted on by alkaline ferricyanide; (2) ortho- and para-chloronitrobenzene form the corresponding nitrophenols by interaction with alkalis, whilst the meta compound is not affected; (3) ortho- and para-ethoxynitrobenzene are converted into the corresponding nitranilines on treatment with ammonia, but the meta-derivative is not affected. The authors consider that these facts are in complete accordance with the view of substitution advocated by one of them (*Trans.*, 1898, 73, 445), namely, that substitution in nitro-compounds is largely due to the occurrence of successive, irreversible, desmotropic changes in products formed by the addition of the acting agent to the side group.

In the hope of showing that when acid oxidising agents act on nitro-compounds, ortho- or para-nitrophenols, if any, would be produced, the authors undertook the investigation of an acid substance formed under certain conditions during the nitration of toluene. As ortho- and para-nitrotoluenes are the chief products of that reaction, it was thought probable that this substance had been formed from one of these. Examination showed, however, that oxidation of toluene had doubtless been the first action, as the substance was identified as dinitroparacresol [$Me : OH : (NO_2)_2 = 1 : 4 : 3 : 5$], and thus contained both nitro-groups in meta-positions relatively to the methyl radicle.

96. "*Hydroxydibromocamphorsulphonic Acid. A Correction.*" By Arthur Lapworth, D.Sc., and F. Stanley Kipping, D.Sc., F.R.S.

In a paper on "Sulphocamphoric Acid and other Derivatives of Camphorsulphonic Acid" the authors described as "hydroxydibromocamphorsulphonic acid, $C_{10}H_{14}Br_2SO_5$," a compound obtained by oxidising ammonium *a*-bromocamphorsulphonate with nitric acid (*Trans.*, 1897, 71, 19). This composition was assigned to the oxidation product in question, partly from the results of analyses, partly from the study of a well-defined crystalline sulpholactone, $C_{10}H_{12}Br_2SO_4$, which was obtained simultaneously with the acid, and into which the acid was found to be convertible under certain specified conditions. At the same time, it was admitted that no direct evidence of the presence of a hydroxyl group in the acid had been obtained, and that, although the conversion of the acid into the lactone had been accomplished, the method by which this change was brought about was difficult to explain.

Further investigation has shown that the supposed "hydroxy-acid, $C_{10}H_{14}Br_2SO_5$," is in reality a *hydrated dibromocamphorsulphonic acid*, $C_{10}H_{14}Br_2SO_4,H_2O$, so that its conversion into the lactone by the process employed (boiling with aqueous silver nitrate) is now explained as a simple oxidation followed by elimination of the elements of water. The analyses already referred to gave results agreeing just as well with those required by the new ($C=29·4$; $H=3·9$; $Br=39·2$; $S=7·8$ per cent) as with those calculated for the original formula, and further analyses have given equally satisfactory results ($C=29·7$; $H=3·8$; $Br=39·4$). The *anhydrous acid* was only obtained with difficulty owing to the water of crystallisation in the hydrated compound being very obstinately retained; it crystallised from petroleum and ether in slender prisms melting with decomposition at 245—252°, and on analysis gave the following results ($C_{10}H_{14}Br_2SO_4$ requires $C=30·8$; $H=3·6$; $Br=41·0$. Found $C=30·5$; $H=3·6$; $Br=41·2$ per cent).

One of the authors has now obtained the acid by a method which confirms this view of its composition, and its investigation is being continued.

97. "*Enantiomorphism.*" By F. Stanley Kipping, D.Sc., F.R.S., and William Jackson Pope.

The authors have previously shown (*Proc.*, 1896, 12, 249) that, on crystallising the cubic tetartohedral sodium chlorate from aqueous solutions containing various optically active carbohydrates, the two enantiomorphously related crystalline forms of sodium chlorate are deposited in different numbers; numerical data respecting the ratios of the numbers in which dextro- and lævo-crystals of sodium chlorate separate from solutions containing dextroglucose, mannitol, dulcitol, and isodulcitol are now given. A saturated solution of sodium chlorate containing 200 grms. of *d*-glucose per litre deposits on crystallisation an average of 31·75 per cent of dextro- and 68·25 per cent of lævo-crystals of sodium chlorate by number; results showing that a similar enantiomorphous influence is exercised on the crystallisation of sodium chlorate by other carbohydrates are also given.

Data have also been obtained respecting the proportion in which dextro- and lævo-crystals of sodium chlorate separate from pure aqueous solutions; the examination of a large number of crops of crystals shows that $50·08 \pm 0·11$ per cent of the deposited crystals are dextrorotatory.

98. "*Azobenzene Derivatives of Chrysin, Euxanthone, Gentisin, and Morin.*" By A. G. Perkin.

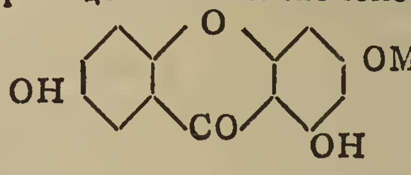
It has been previously shown that apigenin, the colouring matter of parsley, *Apium petroselinum* (*Trans.*, 1897, 71, 805), forms a disazo-derivative, and that during its purification with nitrobenzene and acetic a by-product is obtained, which is evidently an acetyl compound (*Proc.* 1897, 13, 54). Thus prepared, the latter is apt to be impure, and is best formed by the prolonged digestion of disazo-benzeneapigenin with boiling acetic anhydride. It forms orange-red needles melting at 277—280° when rapidly heated, and in general properties is almost indistinguishable from the disazo-compound itself.

Chrysin, the colouring matter of poplar buds, yields a *disazo*-derivative, $C_{15}H_8O_4(N_2Ph)_2$, which crystallises in orange-coloured needles, melts at 250—252°, and is insoluble in alkaline solutions. It contains no free hydroxyl groups.

The diazobenzene groups in these compounds are thus adjacent to the two hydroxyl radicles of the phloroglucinol nucleus, and the results harmonise with previous work which indicated that apigenin is a hydroxychrysin.

Euxanthone, derived from the Indian dye-stuff "purree," yields *disazobenzene-euxanthone*, $C_{13}H_6O_4(N_2Ph)_2$, which crystallises in brick-red needles, melts at 249—250°, and is almost insoluble in alkalis. Acetic anhydride converts it into a *diacetyl* compound, $C_{13}H_4O_4Ac_2(N_2Ph)_2$, which forms olive-coloured needles and melts at 197—199°.

From gentisin, *disazobenzenegentisin*, $C_{14}H_8O_5(N_2Ph)_2$, is obtained. This crystallises in orange-red needles, melts at 218—220°, and yields a *diacetyl* derivative, $C_{14}H_6O_5Ac_2(N_2Ph)_2$. These results indicate that the methoxyl group in gentisin has the following position:—



Disazobenzenemorin, $C_{15}H_8O_7(N_2Ph)_2$, a red-brown, crystalline powder, is formed in very small quantity by the interaction of diazobenzene sulphate with morin in alkaline solution. No trisazo-compound could be obtained.

99. "*Constituents of the Indian Dyestuff 'Waras.'*" By A. G. Perkin.

Waras is a purplish powder which covers the seed pods of *Flemingia congesta*, an erect, woody shrub of Africa and India. In its general properties and microscopic appearance it closely resembles kamala (*Mallotus Philippinensis*) previously investigated (*Trans.*, 1893, 63, 975; 1894, 65, 232). For the supply of material, which is very difficult to procure, the author is indebted to the authorities of the Imperial Institute.

Flemingin, $C_{12}H_{12}O_3$, the principal crystalline constituent, was obtained as an orange-red powder consisting of small, prismatic needles melting at 171—172°. In appearance and numerous properties it resembles the rottlerin of kamala, but is distinguished from this by its solubility in alcohol, and by the browner tint of its alkaline solutions. In an alkaline bath, it dies silk a golden yellow, and is a stronger dyestuff than rottlerin. On fusion with alkali, it gave acetic acid, salicylic acid, and an acid of higher melting point which was not identified.

Homoflemingin (C=69·97; H=5·75), present only in minute quantity, forms glistening, yellow needles, melts at 164—166°, and possesses properties resembling those of flemingin.

The *resin of high melting point*, ($C_{12}H_{12}O_3$, forms a brick-red powder soluble in alkali, with a deep brown tint, and yields acetic and salicylic acids on fusion with alkali. It dies silk in shades which are redder than those produced by flemingin.

The *resin of low melting point*, $C_{13}H_{14}O_3$, is a deep orange-brown, transparent mass which melts below 100°, is soluble in alkali with an orange-brown colour, and closely resembles the resin of low melting point of kamala. On fusion with alkali, acetic and salicylic acids are obtained, and on boiling with nitric acid (sp. gr. 1·5) oxalic acid is formed.

From numerous characteristic reactions described in the paper, it is concluded that the above substances are closely related to, though not identical with, those present in kamala.

Waras dyes silk a golden yellow shade, and is a much stronger dye-stuff than kamala.

100. "*Note on the Oxidation of Charcoal by Nitric Acid.*" By G. Dickson, M.A., and T. H. Easterfield, M.A., Ph.D.

Well-burnt charcoal reacts readily with fuming nitric acid, the action being accompanied by a considerable rise of temperature. When boiled for 24 hours with fuming nitric acid, the charcoal goes entirely into solution, and on dilution with water a black, amorphous substance is precipitated, whilst mellitic and non-crystalline acids remain in solution. The black, amorphous substance resembles the "mellogen" of Bartoli and Papasogli (*Gazz.*, 1882, 12, 117), it is easily soluble in alkali, and on oxidation by alkaline permanganate yields oxalic and mellitic acids in about equal proportions.

From charcoal, 25 per cent. of its weight of crystalline ammonium mellitate can be obtained by the following process. The charcoal is boiled with fuming nitric acid for 24 hours and further oxidised by adding potassium chlorate to the boiling solution; the organic acids, after precipitation as barium salts, are converted into ammonium salts. The yield of mellitic acid varies only slightly, whether the charcoal contains 2 or only 0·2 per cent of hydrogen. Coal under similar conditions gives only a small yield of mellitic acid.

Even nitric acid of sp. gr. 1·1 can oxidise well-burnt charcoal. After boiling continuously for seven days, the charcoal is changed to a black, impalpable mud, soluble in alkali. The nitric acid solution contains mellitic but no oxalic acid.

Banquet to Past Presidents.

The banquet to Past Presidents, unavoidably postponed from June 9th, has been finally fixed by the Council for Friday, November 11th.

Royal Institution.—A General Monthly Meeting was held on the 4th inst., Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, presiding. The special thanks of the Members were returned for the following donations to the Fund for the Promotion of Experimental Research at Low Temperatures:—Sir Frederick Abel, Bart., K.C.B., £100; Sir Andrew Noble, K.C.B., £100; Sir John Brunner, Bart., M.P., £50.

CORRESPONDENCE.

THE NEW GASES.

To the Editor of the Chemical News.

Sir,—In a paper read before the Royal Society on June 16th, by Prof. Ramsay and Mr. Travers, in describing a supposed new gas, they mention the existence of a brilliant yellow line not identical with sodium, helium, or krypton, having a wave-length of 5849·6: this line they call D_5, and propose the name "neon" for the element which it indicates.

Now, in the *Comptes Rendus* (cxxvi., p. 1762), in a paper by Messrs. Ramsay and Travers, the same line D_5, wave-length 5849·6, is again described, but in this case they propose the name "metargon" for the new gas. Surely there must be a misprint in one paper or the other. In the Royal Society paper both "neon" and "metargon" are fully described, and a number of lines with their wave-lengths are given for each gas; but in the *Comptes Rendus* paper "neon" is passed over very lightly, and practically all the figures given refer to what is there called "metargon." These discrepancies are further accentuated by the densities given: in the Royal Society paper, the gas with the line D_5 called "neon" is given a density of 14·67; while in the *Comptes Rendus* paper, the gas with the line D_5 called "metargon" has a density of 19·87. It is obvious that D_5, wave-length 5849·6, cannot belong to both gases. To which does it belong?—I am, &c.,

Puzzled.

THE NEW GASES.

To the Editor of the Chemical News.

Sir,—In 1892 Dr. Hussein Off and I read before the Chemical Society a paper (4½ pages long) entitled "Indications of a possible New Element in an Egyptian Mineral," and this was the only commmunication on the subject that I wrote or was responsible for; a description of this as "an elaborate paper to announce the discovery of a new element" is hardly accurate.

It is still more inaccurate to say that Prof. Ramsay has nothing to show as to the existence of the new gases but spectral lines, and this is the whole basis of "Suum Cuique's" attack: reference to the papers of Prof. Ramsay and his colleagues show that the attempts made to split up the new gases have revealed properties sufficient without the spectra to afford strong evidence that the gases are really new. Propositions with an inaccurate basis need no assailing; they fail naturally.

I believe the impression that I had gathered, that Prof. Ramsay had the possible mixed nature of argon constantly before his mind, to be correct; if not, why should he have worked so assiduously, and, as we now learn, successfully, to split it up? I have no difficulty in reconciling this impression with the fact that argon was declared to be an element. This is but an instance of the inadequacy of language to express ideas; we have defined an element as a body which has not, by any possible means in our power, been split up, and argon, when it was declared to be an element, conformed strictly to that definition. We do not vilify the early workers on didymium. We all accept the expression "elements in an impure state" as a reasonable phrase, and these words imply the acceptance of the possibility of an element being mixed with other substances, though not losing thereby its elementary character.

It appears that, in his first letter, when "Suum Cuique" was only considering Prof. Ramsay's work, he could see no merit in the discovery of argon; in his second letter, after being reminded of Lord Rayleigh's share, he admits that there is much merit. It is further stated that Prof. Ramsay is not the chemist with whom Lord Rayleigh would have associated himself had he been left a free agent. It looks very much as if Prof. Ramsay's scientific work is to be belittled, because exception is taken to his conduct from an ethical standpoint. Would it not be more manly to state any real grounds of complaint that may exist, than to assail his work inaccurately and anonymously?

I regret that I made the groundless and utterly erroneous assumption that "Suum Cuique" was not acquainted with the classical experiment of Cavendish; seeing that it is by no means the best known of his experiments, I imagined that probability was against his having known it. I am sorry that, in attributing ignorance to him, I used the unnecessary word "blissfully," and admit that the annoyance I must have caused him justifies his free use of adjectives.

In conclusion, Sir, I hope, as a student of Prof. Ramsay's work, that he and his colleague will not be led by this discussion to defer publication of any more results till they have isolated all the gases of the atmosphere in a state of absolute purity, and have determined the whole of their properties: I believe I shall voice the opinion of a considerable section, if I say that the publication of their results as they get them will be welcomed as an addition to the world's knowledge.—I am, &c.,

H. Droop Richmond.

St. Margaret's, July 5, 1898.

MOLECULAR DETERMINATIONS IN SOLUTIONS.

To the Editor of the Chemical News.

Sir,—If it be the case, as mentioned in the paper by Messrs. Jones and King (Chemical News, lxxvii., p. 243), that the boiling-point method is the only one at present applicable to the generality of solvents, it may doubtless be of interest to describe a process which under some circumstances may be found useful. I tested it some time ago with satisfactory results. It is generally applicable to all, or at all events to the more volatile solvents, not limited strictly to one particular temperature, but workable for a considerable range below the boiling-points. It is independent of any constants special to different liquids. It is, moreover, capable of being applied rapidly, and with no further equipment than is found in every laboratory.

The principle of the method is the measurement of vapour pressure by means of evaporation. With a liquid evaporating, the number of vapour molecules per unit volume of the space above will be proportional to the pressure of the vapour. If the space—*i.e.*, if the air—above the liquid is renewed as fast as saturated, the number of molecules carried off will be proportional to the vapour pressure. This will also be true when different liquids are compared, and when a pure liquid is compared with the same liquid containing a non-volatile dissolved substance. The presence of substances in solution lowers the pressure, the amount evaporated is diminished, the diminution of the quantity evaporated is a measure of the diminution of pressure.

To apply this in practice it is, of course, not sufficient simply to leave the pure liquid and the solution to evaporate under similar conditions of pressure, temperature, and extent of exposed surface. The changes of concentration at the surface of the solution are too tardily counteracted by diffusion; the decrement of evaporation is far greater than it would be if the process were simply determined by the average concentration.

A uniform concentration throughout the liquid and a uniform evaporation, however, can be secured by blowing through the solution and the pure solvent approximately equal quantities of air.

A process of this sort, described by Ostwald, was put in practice by Walker, and by Will and Bredig, but it involves too great an expenditure of time; even for a liquid as volatile as alcohol a single experiment occupied twenty-four hours.

By the method here described a single experiment occupies, when once the apparatus has been constructed, about twenty minutes, and it can be repeated in ten. It consists of a couple of well-corked test-tubes, each fitted like a Woulff's bottle, with a tube dipping nearly to the bottom, and a short outlet tube with one bend; in one of these test-tubes is placed the solution, in the other the pure solvent. One of the outlet tubes is put in communication with an aspirator, and the dipping-tube of the other test-tube in communication with the air-cistern—a closed vessel into which the water of the aspirator is allowed to run. Thus a current of air is drawn through the liquid in the one test-tube and driven through the other, the quantities of air in each case being approximately equal. This approximation is sufficiently exact when by changing the connections the current, under the same conditions, has been reversed. The difference still remaining is due to the difference of vapour pressure between the two liquids, and it may be got over by saturating the air with the pure liquid, as under aspiration it issues from the test-tube containing the dissolved substance. The advantage seemed, however, on trial to be more theoretical than practical.

The temperature was kept uniform by means of a (generally cold) water-bath, in which the test-tubes stood. To keep them dry, for greater convenience and correctness of weighing, they were surrounded by two close-fitting cylinders of thin copper, blocked at the bottom, which were inserted in the closed top of the water-bath; thus the test-tubes were not in contact with water or water-vapour.

The test-tubes were fitted with rubber corks of two holes; but in the case of carbon disulphide, benzene, and such solvents as rapidly pass through indiarubber, these had to be replaced by ordinary corks capped with sealing-wax. The weighing of the test-tubes and contents was done with the corks and glass fittings *in situ*. Special precautions in the case of volatile solvents had to be taken with the capping of the small glass tubes. Part of an old Kipp's apparatus was extremely serviceable as aspirator; the construction enabled the amount of water passed to be very accurately controlled.

For water and liquids of low volatility the whole of the water-bath with the test-tube should be put in a water-oven, and so arranged that the connections can be changed on the outside. This will prevent the solvent from condensing on the outlet tubes, which it would otherwise do if only the water-bath were heated.

With such apparatus, when both test-tubes are charged with the pure solvent the difference of the amount evaporated ought not to differ by 1/10th per cent. For the purpose of the experiment the air passing must be saturated. This renders the application of heat necessary in the case of liquids of non-volatility equal to toluene. For such a liquid as carbon disulphide it made no difference whether the dipping-tubes passed 9 c.m. or 1·5 c.m. into the liquid; but, of course, for the sake of equalising the pressure, both dipping-tubes should go to the same depth (they may be graduated for the purpose). This question of pressure seems to prevent the use of *two blow-throughs*,—with one suction arrangement and one *blow-through* it is greatly neutralised.

Where advisable it is possible to substitute any other gas for air. Of course the air must be dried as it passes from the air-cistern. The rate of air-flow is without effect on the result, but splashing inside the test-tubes must be avoided.

Of course the concentration of the solution varies during the experiment, the average concentration has to be calculated for. Not more than 1/10th of the whole solution need generally be evaporated.

The formula for calculation will be as follows :—

$$\frac{\text{Difference of amount evaporated in the two tubes.}}{\text{Amount evaporated in the solution.}} = \frac{\text{Number of molecules of dissolved substance.}}{\text{Number of molecules used to dissolve it.}}$$

Or if q be the amount evaporated from the pure solvent, q' the amount evaporated from the solution, N the number of gramme-molecules of solvent in the solution, n the number of gramme-molecules of the dissolved substance—

$$\frac{q - q'}{q'} = \frac{n}{N}$$

There is no constant to be varied for each liquid.

I offer this method to your readers believing that it supplies a rapid and sufficiently accurate means of determining molecular weight, and that from its nature it is also capable of development and improvement so as to attain to the very highest accuracy.—I am, &c,,

P. J. Beveridge, M.A., B.Sc.

St. Helen's, June 28, 1898.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvi., No. 19, May 9, 1898.

Method for the Detection and Estimation of Carbonic Oxide in the presence of Traces of Carburised Gas in the Atmosphere.—Armand Gautier.—To determine the amount of carbonic oxide in air, the air, previously deprived of all dust, acid gases, and water, is passed through two tubes, the first 0·28 m. in length, containing iodic anhydride, and the second 0·18 m. long, containing pure powdered copper (reduced by hydrogen): these tubes are sealed together in such a manner that they can both be placed in an air-oven and heated to 100—105°. This amount of copper is quite sufficient to take up all the iodine given off, no matter how dilute the vapour may be. A number of experiments which follow show that this method is sure and convenient in the ordinary cases when the air, or other inert gas, contains not more than 1/10,000th part of carbonic oxide. But the figures given, however satisfactory they may be in an ordinary case, may not be so certain when there is only a trace of carbonic acid present. To settle this point another potash tube was added at the end of the copper tube for the purpose of collecting the last traces of iodine, and then, for eight hours, a quantity of air containing enough CO_2 to set free nearly 15 m.grms. of iodine was slowly circulated through the apparatus.

The iodide stopped by the copper
was .. .. = 14·72 m.grms.
And that which passed the copper,
but was stopped by the potash,
was .. .. = 0·011 „

The author then goes on to describe further experiments for the purpose of eliminating any hydrocarbides which may be present.

Vaporisation of Iron at the Ordinary Temperatures.—H. Pellat.—The following experiment whs made by the author:—A small iron ring was laid directly on the sensitive surface of a bromo-gelatin plate; at its side another similar ring was placed, but separated from the sensitive surface by a very thin sheet of microscopic *cover* glass; the latter was covered by a bell-jar fastened to the plate with paraffin as in M. Becquerel's sxperiment. The whole was left in the dark from December 24, 1897, until April 27, 1898. After developing the plate, it was found that the iron ring under the jar had made no impression, but that the ring placed directly on the sensitive film had produced an image of a slightly larger size than the ring itself, and therefore extending beyond the line of contact. This experiment shows that the phenomenon is not due to radiations, but to a volatile body produced by the iron.

On a Borocarbide of Glucinum.—P. Lebeau.—Already inserted in full.

Some Halogen Salts of Lead.—V. Thomas.—The object of this note is the study of the chloroiodides of lead. The action of boiling hydrochloric acid on iodide of lead always gives rise to a chloroiodide, PbICl. If iodide of lead reacts on a chloride, or chloride of lead on an iodide, the result is always the same,—PbICl is formed. The existence of the chloroiodide as a well-defined chemical compound is shown by the product of oxidation it is able to form when treated with peroxide of nitrogen.

Thermic Data relating to Ethyl-malonic Acid. Comparison with its Isomers, Glutaric and Methyl-succinic Acids.—G. Massol.—Anhydrous ethyl-malonic acid dissolves in water with a heat of absorption of −2·96 cals. The heats of neutralisation are—for $C_5H_7O_4K$, +14·08 cals., and for $C_5H_6O_4K_2$, +13·80 cals. The heat of formation of a solid neutral salt, from the solid acid and base, is—

$$C_5H_8O_4 \text{ sol.} + 2KOH \text{ sol.} = C_5H_6O_4K_2 \text{ sol.} + 2H_2O \text{ sol.} + 48{\cdot}25 \text{ cals.}$$

The comparison of the values of the three isomers shows that the *acidimetric value* measured thermically by *the heat of formation of a solid neutral potash salt*, varies for each of the three isomers:—

Position 1 : 3 ethyl-malonic acid + 48·25 cals.
„ 1 : 4 methyl-succinic acid + 45·18 „
„ 1 : 5 normal-glutaric acid + 44·23 „

Formation of Furfurol by Cellulose, and its Oxy- and Hydro-derivatives. — Leo Vignon. — The author took equal weights of pure cotton cellulose, and submitted them respectively to the action of (1) acids, (2) oxidising agents, and (3) reducing agents. He obtained three substances; these were left in contact with a cold solution of caustic potash, at 10° B. for five hours; the first and third gave a colourless liquid, the second one a liquid of a pale yellow golden colour; after washing and drying it was found that Nos. 1 and 3 had undergone a loss of weight of 15 per cent, and No. 2 of 25 per cent. Thus oxycellulose is distinctly different from hydro-cellulose, which appears to be identical with hydrogenised cellulose. These were then submitted to the action of boiling hydrochloric acid at 1·06 density, and the furfurol obtained was estimated in the distillate collected, and transformed by phenylhydrazin into hydrazone, according to the following equation:—

$$C_5H_4O_2 + C_6H_5N_2H_3 = C_5H_4ON_2HC_6H_5 + H_2O.$$

Berichte der Deutschen Chemischen Gesellschaft. December 13, 1897.

Organic Derivatives of Selenium.—A. Michaelis and A. Kunckell.—By acting on the ether oxides of naphthol, on the phenols, and the ketones by $SeCl_3$ various compounds are formed. The reactions take place in the cold in ethereal solution; it is fairly energetic. $2CH_3-O.C_{10}H_7+SeCl_2=(CH_3O.C_{10}H_6)2Se+2HCl$; this compound is a reddish crystalline mass, soluble in $CHCl_3$, melting at 138°. The action of $SeCl_2$ on phenol gives a red mass having the formula $Se(C_6H_4.OH)_2$.

Some Organic Derivatives of Tellurium.—E. Rust.—Tetrachloride of tellurium reacts on anisol, giving

$TeCl_2(C_6H_4.OClH_3)_2$, in yellow needles melting at 190°, soluble in ether, benzene, HCl, and the alkalis. The chloroplatinate appears in the form of brown needles, soluble in water and alkalis. The hydrate, bromide, iodide, and nitrate have also been obtained and described. Tetrachloride of tellurium also reacts on phenetol, phenol, and resorcine.

Antimonic Derivatives of Anisol aed Phenetol.—C. Loeloff.—These derivatives are obtained (1) by the action of Na on a mixture of $SbCl_3$ and bromanisol or bromophenetol; (2) by the action of bromanisol on antimoniate of soda. A large number of derivatives are described.

On some Aromatic Compounds containing Bismuth.—A. Gillmeister.—Iodine acts on bismuth-triphenyl in ethereal solution, giving the oxyiodide of bismuth. The iodide, $(C_6H_5)_2BiI$ is obtained by treating an alkaline solution of the chlorine, $(C_6H_5)_3BiCl_2$, by KI. $HgCl_2$ reacts on an alkaline solution of bismuth-triphenyl, giving BiOCl, benzene, and chloromercurate of phenyl. A mixture of nitric and sulphuric acids completely decomposes bismuth-triphenyl into nitrate of bismuth and ortho-dinitrobenzene.

On some Dissymmetric Substituted Phenylhydrazines and their Derivatives.—A. Michaelis.—A certain number of substituted $\alpha\beta$-phenylhydrazines have been prepared by acting on the soda derivative of phenylhydrazine with the alcoholic bromides; the reaction takes place on the water-bath in the presence of benzene. The author describes the hydrochlorate of α-ethyl-phenylhydrazine, ethylindolcarbonic acid, dichlorethyloxindol, dibromethyloxindol, and many other bodies and their derivatives.

Action of Chloroform and Alcoholic Potash on Phenylhydrazine.—S. Ruhemann.—The action of nitric acid on diphenyltetrazoline furnishes two nitrated derivatives, one of which melts above 300° and is difficultly soluble in acetic acid. By reducing it by warm $SnCl_2$ and HCl an amidodiphenyltetrazoline is obtained, crystallising in white needles, fusible at 188°, and soluble in alcohol.

NOTES AND QUERIES,

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Decolourising Oils.—(Reply to H. Matthews).—Decolourising oils is a rather incorrect expression. There is no process for bleaching rape oils or oils for lubricating purposes; they are rendered paler, but they are not decolourised. This result can be attained by ozone, which at the same time thickens the oil. Dark low-grade fats are transformed into a yellowish material without the use of acid.—Em. Andreoli.

Physics of Gases.—Could any of your readers inform me, through your "Notes and Queries" column, if there is any work or works from which I could learn something of the boiling- or liquefying-points of gases (including air), their behaviour under very high pressures, and also their influence or action upon metals. Said works should be as free as possible from technical terms and mathematics. I most particularly desire to know the behaviour under high pressures. Please state prices and publishers.—Engineering Student of Physics.

Erratum.—Vol. lxxvii., p. 263, col 1, line 2 of the paragraph commencing "At the regular meeting," *for* "Breyer and Schweitzer" *read* "Frear and Sweetser."

THE CHEMICAL NEWS.

Vol. LXXVIII., No. 2016.

ON THE

POSITION OF HELIUM, ARGON, AND KRYPTON IN THE SCHEME OF ELEMENTS.[*]

By Sir WILLIAM CROOKES, F.R.S.

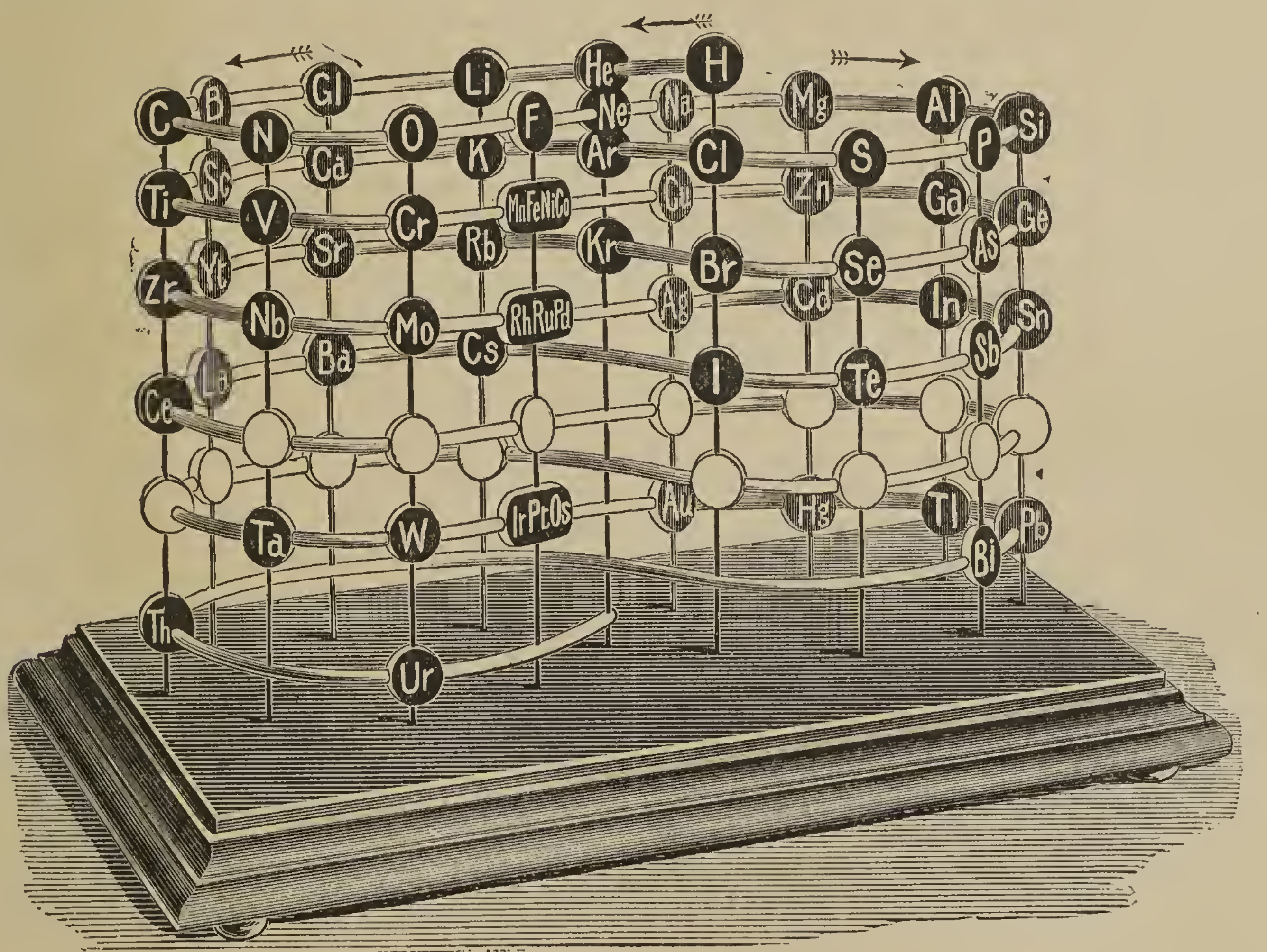
It has been found difficult to give the elements argon and helium (and I think the same difficulty will exist in respect to the gas krypton) their proper place in the scheme of arrangement of the elements which we owe to the ingenuity and scientific acumen of Newlands, Mendeléef, and others. Some years ago, carrying a little further Professor Emerson Reynolds's idea of representing the scheme of elements by a zigzag line, I thought of projecting a scheme in three dimensional space, and exhibited at one of the meetings of the Chemical Society[†] a model illustrating my views. Since that time, I have re-arranged the positions then assigned to some of the less known elements in accordance with later atomic weight determinations, and thereby made the curve more symmetrical.

Many of the elemental facts can be well explained by supposing the space projection of the scheme of elements to be a spiral. This curve is, however, inadmissible, inasmuch, as the curve has to pass through a point neutral as to electricity and chemical energy twice in each cycle. We must, therefore, adopt some other figure. A figure-of-eight will foreshorten into a zigzag as well as a spiral, and it fulfils every condition of the problem. Such a figure will result from three very simple simultaneous motions. First, an oscillation to and fro (suppose east and west); secondly, an oscillation at right angles to the former (suppose north and south), and thirdly, a motion at right angles to these two (suppose downwards), which, in its simplest form, would be with unvarying velocity.

I take any arbitrary and convenient figure-of-eight, without reference to its exact nature; I divide each of the loops into eight equal parts, and then drop from these points ordinates corresponding to the atomic weights of the first cycle of elements. I have here a model representing this figure projected in space; in it the elements are supposed to follow one another at equal distances along the figure-of-eight spiral, a gap of one division being left at the point of crossing. The vertical height is divided into 240 equal parts on which the atomic weights are plotted, from H = 1 to Ur = 239·59. Each black disc represents an element, and is accurately on a level with its atomic weight on the vertical scale.

The accompanying figure, photographed from the solid model, illustrates the proposed arrangement. The elements falling one under the other along each of the vertical ordinates are shown in the Table.

H	He	Li	Gl	B	C	N	O	F	Na	Mg	Al	Si	P	S
Cl	Ar	K	Ca	Sc	Ti	V	Cr	Mn·Fe·Ni·Co	Cu	Zn	Ga	Ge	As	Se
Br	Kr	Rb	Sr	Yt	Zr	Nb	Mo	Rh·Ru·Pd	Ag	Cd	In	Sn	Sb	Te
I	—	Cs	Ba	La	Ce	( )	( )	( )	( )	( )	( )	( )	( )	( )
( )	—	( )	( )	( )	( )	Ta	W	Ir·Pt·Os	Au	Hg	Tl	Pb	Bi	—
—	—	—	—	—	Th	—	Ur	—	—	—	—	—	—	—



The bracketed spaces between cerium and tantalum are probably occupied by elements of the didymium and erbium groups. Their chemical properties are not known with sufficient accuracy to enable their positions to be well defined. They all give coloured absorption spectra and have atomic weights between these limits. Positions marked by a dash (—) are waiting for future discoveries to fill up.

Let me suppose that at the birth of the elements, as we now know them, the action of the *vis generatrix* might be diagrammatically represented by a journey to and fro in

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[*] A Paper read before the Royal Society, June 9, 1898.

[†] Presidential Address to the Chemical Society, March 28, 1888.

cycles along a figure-of-eight path, while, simultaneously time is flowing on, and some circumstance by which the element-forming cause is conditioned (*e.g.*, temperature) is declining; (variations which I have endeavoured to represent by the downward slope.) The result of the first cycle may be represented in the diagram by supposing that the unknown formative cause has scattered along its journey the groupings now called hydrogen, lithium, glucinum, boron, carbon, nitrogen, oxygen, fluorine, sodium, magnesium, aluminium, silicon, phosphorus, sulphur, and chlorine. But the swing of the pendulum is not arrested at the end of the first round. It still proceeds on its journey, and had the conditions remained constant, the next elementary grouping generated would again be lithium, and the original cycle would eternally reappear, producing again and again the same fourteen elements. But the conditions are not quite the same. Those represented by the two mutually rectangular horizontal components of the motion (say chemical and electrical energy) are not materially modified; that to which the vertical component corresponds has lessened, and so, instead of lithium being repeated by lithium, the groupings which form the commencement of the second cycle are not lithium, but its lineal descendant, potassium.

It is seen that each coil of the lemniscate track crosses the neutral line at lower and lower points. This line is neutral as to electricity, and neutral as to chemical action. Electro-positive elements are generated on the northerly or retreating half of the swing, and electro-negative elements on the southerly or approaching half. Chemical atomicity is governed by distance from the central point of neutrality; monatomic elements being one remove from it, diatomic elements two removes, and so on. Paramagnetic elements congregate to the left of the neutral line, and diamagnetic elements to the right. With few exceptions, all the most metallic elements lie on the north.

Till recently chemists knew no element which had not more or less marked chemical properties, but now by the researches of Lord Rayleigh and Professor Ramsay, we are brought face to face with a group of bodies with apparently no chemical properties, forming an exception to the other chemical elements. I venture to suggest that these elements, helium, argon, and krypton, in this scheme naturally fall into their places as they stand on the neutral line. Helium, with an atomic weight of 4, fits into the neutral position between hydrogen and lithium. Argon with an atomic weight of about 40, as naturally falls into the neutral position between chlorine and potassium. While krypton with an atomic weight of about 80, will find a place between bromine and rubidium.

See how well the analogous elements follow one another in order: C, Ti, and Zr; N and V; Gl, Ca, Sr, and Ba; Li, K, Rb, and Cs; Cl, Br, and I; S, Se, and Te; Mg, Zn, Cd, and Hg; P, As, Sb, and Bi; Al, Ga, In, and Tl. The symmetry of these series shows that we are on the right track. It also shows how many missing elements are waiting for discovery, and it would not now be impossible to emulate the brilliant feat of Mendeléef in the celebrated cases of Eka-silicon and Eka-aluminium. Along the neutral line alone are places for many more bodies, which will probably increase in density and atomic weight until we come to inert bodies in the solid form.

Four groups are seen under one another, each consisting of closely allied elements which Professor Mendeléef has relegated to his 8th family. They congregate round the atomic weight 57, manganese, iron, nickel, and cobalt; round the atomic weight 103, ruthenium, rhodium, and palladium; while lower down round atomic weight 195 are congregated osmium, iridium, and platinum. These groups are interperiodic because their atomic weights exclude them from the small periods into which the other elements fall; and because their chemical relations with some members of the neighbouring groups show that they are interperiodic in the sense of being formed in transition stages.

Note, June 22, 1898.—Since the above was written, Professor Ramsay and Mr. Travers have discovered two other inert gases accompanying argon in the atmosphere. These are called Neon and Metargon. From data supplied me by Professor Ramsay, it is probable that neon has an atomic weight of about 22, which would bring it into the neutral position between fluorine and sodium. Metargon is said to have an atomic weight of about 40; if so, it shares the third neutral position with argon. I have marked the positions of these new elements on the diagram.

SOME OBSERVATIONS ON A PAPER BY MESSRS. DUNSTAN AND HENRY ENTITLED "A CHEMICAL INVESTIGATION OF THE CONSTITUENTS OF INDIAN AND AMERICAN PODOPHYLLUM."

By F. B. POWER, Ph.D., F.C.S.

In a paper published in the *Journal of the Chemical Society*, April, 1898, pp. 209—226, bearing the above-mentioned title, there are some errors and omissions which ought to be corrected. On page 209 the authors make the following statement:—"The chemical constituents of the rhizome of the American Podophyllum peltatum have, however, been made the subject of several investigations. First, in 1832, Hodgson prepared the mixture of resins known and largely used in medicine as 'podophyllin' by precipitating a concentrated alcoholic extract of the rhizome with water; this is now manufactured on a large scale, and is the form in which 'podophyllum' is usually administered as a drug. *The first important contribution to the chemistry of Podophyllum was that made by Podwyssotski* (*Pharm. Journ.* (iii.), 12, pp. 217, 1011). *This chemist showed that the rhizome did not, as was previously supposed, contain the alkaloid berberine.*"

From this statement the inference would naturally be drawn that Podwyssotski was the first to prove the absence of berberine in Podophyllum.

The absence of berberine, or any other alkaloid, in Podophyllum was first conclusively proved and recorded by me in 1877, or four years before the publication of Podwyssotski's first paper on Podophyllum, as may be seen from the following extract from the *Proc. Amer. Pharm. Assoc.*, 1877, p. 425:—"The rhizome of Podophyllum peltatum contains *no* berberine, and the colouring matter is a constituent of the resin itself; a fact all the more surprising when we consider that for a period of nearly half a century the supposed presence of this alkaloid in the rhizome should have become so universally accepted; and from time to time confirmed, without ever having been isolated from it." And again (*loc. cit.*, p. 433), "to briefly summarise the results of these experiments, it may finally be observed that Podophyllum contains no alkaloid, and that the yellow colouring principle heretofore supposed to be due to berberine is due to the resin, and to that portion of it which is of acid character and which may with some degree of propriety receive the previously applied name of podophyllinic acid, which has also in chemical behaviour many analogies to quercitrin."

Podwyssotski, indeed, never claimed to have first shown the absence of berberine in Podophyllum, but simply confirmed my observations that no alkaloid was present. In his chronological review of the investigations preceding his own (see *Pharm. Zeitschrift für Russland*, 1881, p. 888), he refers to a note by Flückiger in the French translation by Lanessan of the first edition of *Pharmaco-*

graphia (*Histoire des Drogues*, 1878, i., p. 90), which is as follows:—"Je ne saurais confirmer la présence de la berberine dans cette racine: je l'en trouve dépourvue.—F.A.F." This note was apparently written at about the time that I was engaged in an investigation of Podophyllum in the laboratory of Professor Flückiger at Strassburg. It is therefore of interest to note what Professor Flückiger has also written on this subject in the *Pharmacographia*, 2nd edition, 1879, p. 38:—"F. F. Mayer, of New York, stated Podophyllum to contain, beside the resin already mentioned, a large proportion of *berberine*, a colourless alkaloid, an odoriferous substance which might be obtained by sublimation in colourless scales, and finally saponin. From all these bodies the resin as prepared by Power was ascertained by him to be destitute; *he especially proved the absence of berberine in Podophyllum.*"

In the "National Dispensatory," 5th edition, 1894, p. 1368, under the title "Resina Podophylli," Professor Maisch has written: "F. B. Power (1877), observed that the largest portion of the resin consists of at least four compounds, differing in their solubility in ether and hot water, and in their behaviour to alkalies, ferric chloride, and lead acetate; fused with potassa *protocatechuic acid was obtained, but no resorcin.*"

And again, under "Podophyllum" (*loc. cit.*, p. 1267), "F. F. Mayer (1863) announced the presence of berberine and another (white) alkaloid, and of saponin, but the investigations of F. B. Power (1877-8) indicate the total *absence of saponin and of any alkaloid*, and we (Professor Maisch) have *subsequently* shown that at all periods of its growth the rhizome is free from alkaloid."

The "United States Dispensatory," 17th edition, p. 1154, states:—"The researches of Power, Maisch, Guareschi, and Podwyssotski have established the fact that Podophyllum does not contain berberine or any alkaloid, and that its activity is due to principles present in the resin."

Also in "Thorpe's Dictionary of Applied Science," 1895, vol. iii., p. 351, under "Podophyllum Resin," we find the following recorded:—"Besides the resin upon which the purgative property of the drug depends, Mayer, who examined Podophyllum in 1863, reported it to contain berberine, saponin, and a colourless alkaloid, but no evidence of these compounds, at least in the crude resin, has been obtained by subsequent observers (Power, *Amer. Journ. Pharm.*, 1878, p. 369; Maisch, *Ibid.*, 1879, p. 590; Biddle, *Pharm. Journ.*, (3), 10, p. 468.)"

"Watts' Dictionary of the Economic Products of India," vi., part 1, p. 301, states under "Podophyllum": —Cadbury, Power, and others affirm that the medicinal virtue is due to the resin soluble in ether, and that the other resin left behind in the alcoholic medium is comparatively inert. The experiments of Power, Maisch, Guareschi, Podwyssotski, and others, prove that Podophyllum does not contain berberine (as was announced by Mayer) or any alkaloid, and that its activity is due to the resin or resins.'

The "Imperial Institute Handbooks of Commercial Products," No. 3, p. 3, under "Podophyllum," reproduces the article from "Watts' Dictionary of Economic Products" as quoted above.

Podwyssotski also did not omit to give credit, for in the *Pharm. Zeitschrift für Russland*, Nov. 1, 1881, No. 44, p. 777, he says:—"Im Anfange der vorleigenden Anhandlung erwähnte ich dass sich mit der Untersuchung des Podophyllins hauptsächlich Buchheim in Deutschland, Power in Amerika, und Guareschi in Italien beschäftigten."

In considering the action of fused potash on podophyllotoxin and on podophylloresin, Messrs. Dunstan and Henry (*loc. cit.*, pp. 216, 222), refer to the investigation of Guareschi, but make no mention of the fact that two years before the publication of Guareschi's paper (*Ber. d. Deutsch. Chem. Ges.*, 1879, p. 683), I had observed and recorded the formation of protocatechuic acid as a product of the action of fused potassium hydroxide on podophyllin (*Proc. Amer. Pharm. Assoc.*, 1877, p. 428), and this point of the investigation was even subsequently extended to ascertain whether protocatechuic acid is a natural constituent of the rhizome of Podophyllum (*Amer. Journ. Pharm.*, 1878, p. 369). By the action of fused potassa on podophyllin it was likewise observed and recorded that volatile acids are formed (*loc. cit.*, p. 428) and by the action of fused potash on Podophyllotoxin, Messrs. Dunstan and Henry have now identified the volatile acid formed as acetic acid.

Although Messrs. Dunstan and Henry may be acceded the privilege of their own opinion in considering the investigation of Podwyssotski to be "the first important contribution to the chemistry of Podophyllum," it is an error to state or to suggest that Podwyssotski was the first to prove "that the rhizome did not, *as was previously supposed*, contain the alkaloid berberine."

It is not desirable at this time to enter into a more extended discussion of the paper by Messrs. Dunstan and Henry, and the interpretation of their results.

AN IMPROVED AND NOVEL FORM OF ACCUMULATOR FOR RAPID AND HEAVY DISCHARGES.

By H. N. WARREN, Principal, Liverpool Research Laboratory.

This energetic secondary, which has been specially designed for experimental purposes where high tension is required, differs from all other forms of accumulators which have been from time to time enumerated throughout the pages of scientific literature, not only as regards the construction of the plates, but also as to the non-sulphating nature of the same. The grids in the first instance, previous to pasting, are so turned by suitable appliances that the positive plate after the operation presents a true cylinder, which is further surrounded by its accompanying negative to within one quarter of the total circumference of the positive cylinder.

Within the positive cylinder is now introduced a second small negative plate, insulated from the surrounding positive and attached to the outside negative, the insulations being carefully effected by means of asbestos.

The entire grids are afterwards transformed into true plates by thoroughly incorporating the perforations of the grids with a paste composed of red lead, litharge, and vitriol, in suitable proportions, the plates thus so far constructed being immediately transferred to the air-bath in order to undergo the (second) process of baking. This process requires the greatest skill on the part of the operator, and, if successfully carried out, a plate taken from the oven whilst still hot should present a surface of sufficient hardness to be with difficulty scratched by means of the point of a knife, and show practically no deterioration when suddenly plunged into cold water,—rather a severe test when compared with other forms of plates, but by no means too severe, as extended experience has shown us, when dealing with rapid discharges.

After the plates have withstood the above tests, they are at once removed to the reducing tanks, and thereby brought to the condition of spongy lead by the reducive action afforded by means of amalgamated zinc in contact with dilute sulphuric acid. The plates thus partially formed, after the necessary process of lixiviation has been bestowed upon them, are mounted in cylindrical fashion, as above described, while the true formation of the plates is now accomplished in the usual manner, using a current corresponding to the square surface presented by the plates in the first instance: at the same time the non-sulphation of the plates is effected by the introduction of certain phosphatic compounds in proportion to the quantity of dilute sulphuric acid employed. The cells thus produced are very quickly re-charged, and also admit of very rough usage.

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ON THE YTTRIC EARTHS CONTAINED IN THE MONAZITE SANDS.

By O. BOUDOUARD.

In a previous paper (*Comptes Rendus*, cxxii., p. 697), in collaboration with the late M. Schützenberger, I predicted the possible existence of a new earth precipitable by oxalic acid, not giving an insoluble double sulphate with the alkaline sulphates, and of which the atomic weight should be about 102. This was only a first indication, and it is the results I have since obtained that I now have the honour of presenting to the Academy.

A. I mixed the oxides of which the atomic weights of the corresponding metals were 102·2, 102·45, 102·6, 103, and 102·4, and dissolved them in nitric acid. The nitrate was transformed into sulphate, and, after the addition of sulphate of potassium to remove the earths of the cerium group (*Comptes Rendus*, cxxvi., p. 900), the yttric earths were precipitated with ammonia. The hydrates after being washed, to get rid of all traces of alkali, were dissolved in nitric acid. This nitrate was submitted to fractional fusion at 325°:—

	Atomic weight.
Sub-nitrate	103·0
Mother-liquors	97·7

The oxide 103, transformed into nitrate and submitted to a fresh fusion, gave—

	Atomic weight.
Sub-nitrate	109·5
Mother-liquors	100·6

Finally, the mother-liquor 97·7, by an analogous fractionation, gave—

	Atomic weight.
Sub-nitrate	98·7
Mother-liquors	97·5

B. In this second series I mixed different oxides, the atomic weights of the corresponding metals varying from 95·1 to 99·1 (the greater part gave figures varying from 98·2 to 99·1). I then applied the above-mentioned treatment to this mixture, and the yttria earths thus obtained were dissolved in nitric acid. The nitrate was submitted to a fractional fusion at 325°, which gave—

	Atomic weight.
Sub-nitrate, No. 1 ..	103·6
„ No. 2 ..	97·5
Mother-liquors	96·7

The sub-nitrate No. 1, submitted to a fresh fusion, was divided into two portions:—

	Atomic weight.
Sub-nitrate, No. 1 ..	108·5
Mother-liquors	98·5

C. I then mixed all the oxides of which the atomic weights of the corresponding metals varied from 96 to 112. I collected about 70 grms. of this mixture.

After having eliminated the earths of the ceric group by sulphate of potassium, the unprecipitated oxides were dissolved in nitric acid, and hyposulphite of soda was added to the neutral solution of the nitrate. A precipitate was formed; the reaction is quicker when the solution is warmed than in the cold. The precipitate is collected on a filter and washed. In the clear solution the excess of alkaline hyposulphite is removed, and the unprecipitated earths are brought to the state of oxalates. I thus obtained 45 grms. of earths precipitable by hyposulphite of sodium, and 25 grms. of earths which were not so precipitable. I am now studying these two fractions. This property of hyposulphite of soda seems to me to be so much the more interesting as Fresenius, in his "Traité de Chemie Qualitative" (eighth French edition, p. 134), states that the salts of yttrium are not precipitated by hyposulphite of soda.

The yttric oxides examined in the above three series give almost colourless solutions, of which the absorption spectrum is very feeble; it is characterised by the following wave-lengths:—

657—663	Very faint	(erbium)
643—639	„	(holmium)
537	„	(holmium)
524—522	Faint	(erbium).

The solutions examined under a thickness of 4 c.m. were saturated; the earth was in the state of sulphate.

If we now compare the results obtained in the first two series, we observe that the minimum atomic weight reached is 96·7, and that the other numbers obtained are in the neighbourhood of 97·5. We are far from the atomic weight of yttrium, which is 89·5.

M. Drossbach (*Berichte*, vol. xxix., No. 15, p. 2452; *Moniteur Quesneville*, May, 1897, p. 351), in examining a monazite, announced the probable existence of an earth with an atomic weight of about 100. He is of the opinion that there is therein a new series of earths in the proportion about 20 to 30 per cent.

MM. Urbain and Budichowski (*Comptes Rendus*, cxxiv., p. 618, and cxxvi., p. 835), in fractionating the acetylacetonates of the yttric earths, and M. Urbain in examining the ethylsulphates, reached a low limit of fractions which could no longer be split up,—a limit which did not go below 95.

These results—later than those of M. Schützenberger and myself, who predicted them—now confirm what we anticipated.

Ought we, from this collection of facts, to conclude that the presence of a new earth is proved? or have we only to deal with a mixture of yttria and of an earth with a higher atomic weight? According to this hypothesis, it is necessary to admit of a mixture of more than 90 parts of yttria to 10 of erbia (average atomic weight 97·6), or of ytterbia (average atomic weight 98·2), or of terbia (average atomic weight 95·7)

Nordenskiöld (*Comptes Rendus*, ciii., p. 795), in 1886, obtained an oxide with a constant atomic weight of 107, which he called *oxide of gadolinium*; he thought that he was authorised to admit that oxide of gadolinium, although not an oxide of a simple body, but a mixture of three isomorphous bodies, even when obtained from minerals altogether different and found in localities very far apart from one another, possesses a constant atomic weight. Is the oxide with the atomic weight 97 an oxide of the same kind?

On the other hand, is it permissible to suppose the existence of a new element very near yttrium? This hypothesis is not untenable; it is sufficient to recall the discussion between M. Lecoq de Boisbaudran and Sir William Crookes (*Comptes Rendus*, cviii., p. 165) on the nature of yttrium.

Sir William Crookes called *yttria* a mixture of earths endowed with varied fluorescence, and of which the elements formed a family of bodies very close together,—species of yttriums, with atomic weights oscillating round about 89; in any case these different yttrias gave the same spark spectra.

M. Lecoq de Boisbaudran called yttria the non-fluorescent earth (which we may suppose to be simple or complex) producing the well-known spectrum, and of which the atomic weight is 89.

To sum up, the process of fractionations (sulphates, nitrates, acetylacetonates, ethyl-sulphates) gives a low limit beyond which no further splitting up takes place; this limit is round about 96.

Is this limit only apparent? This is a point which researches I am now actually engaged on may perhaps elucidate.—*Comptes Rendus*, cxxvi., No. 23, June 6, 1898.

ON THE BOILING-POINT OF LIQUID OZONE.

By L. TROOST.

P. Hautefeuille and J. Chappuis were the first to obtain ozone in the liquid state, in the year 1882; it was of an indigo-blue colour (*Comptes Rendus*, xciv., p. 1249, 1882).

Some experiments relative to the determination of the boiling-point of this liquid were carried out in the year 1887 by M. Olszewski. This experienced *savant*, after having liquefied the ozone in a tube cooled down to −184·4° by liquid oxygen boiling at the atmospheric pressure found that (*Vien. Monats. fur Chem.*, viii., p. 69, 1887) the ozone only volatilises very slowly when in a tube placed in liquid ethylene cooled down to −140°, but that it volatilises very rapidly when the temperature of the ethylene approaches its boiling-point. From this he concluded that the boiling-point of liquid ozone would be about −106°. I determined to fix this temperature with greater precision. For this estimation I used, as a thermometric apparatus, an iron-constantin couple furnishing a curve given by melting ice, by the boiling-points of chloride of methyl alone, or traversed by a rapid current of air, by the temperature of a mixture of solid carbonic acid and of chloride of methyl (the temperatures were taken in these last two cases by means of a thermometer graduated according to the indications of the hydrogen thermometer), by the boiling-point of protoxide of nitrogen, by that of liquid ethylene, by the melting-point of solid ethylene, and by the boiling-point of liquid oxygen at the atmospheric pressure. By means of this apparatus temperatures could be read to less than half a degree.

The ozone was obtained by using a Berthelot ozoniser, kept at about −79° by a mixture of solid carbonic acid and chloride of methyl. The liquefaction is produced in a vertical tube, the lower part of which is immersed in a bath of liquid oxygen, contained in a cylindrical glass vessel with double sides, with the intermediary space exhausted to a Crookes vacuum, as recommended by Prof. Dewar.

The ozone liquefies before reaching that part of the tube which is immersed in the liquid oxygen, at a point situated about 2 c.m. above the level of the bath, thanks to the low temperature due to the oxygen gas coming off.

The liquefied ozone collects in small drops having an oily appearance and not wetting the glass; they fall to the bottom of the tube, where there had already been placed one of the joints of the iron-constantin couple;* the other was kept in melting ice. To determine the boiling-point of liquid ozone, the bath of liquid oxygen was lowered until its free surface was about 3 c.m. below the lower extremity of the tube holding the liquid ozone, and the successive deviations shown by the Deprez-d'Arsonval galvanometer were noted. The deviation, after having slowly diminished, remains steady during the time that the liquid ozone is in a state of ebullition; it then goes down again very rapidly until the joint of the couple reaches the temperature of the oxygen gas at this point.

The stationary deviation, transferred to the curve, corresponds to a temperature of −119°. I have tried this experiment several times, on different quantities of liquid, and I have always obtained the same result.†

We may therefore conclude that the boiling-point of liquid ozone at the atmospheric pressure is −119°.

The liquid oxygen used in these experiments was obtained by means of an apparatus constructed according to the method given by Prof. Dewar—using commercial compressed oxygen cooled down to −79° in a long serpentine tube. In this manner about a quarter of a litre of liquid oxygen can be obtained in the laboratory or the lecture-room in less than half an hour, without the use of pumps or any motive power.—*Comptes Rendus*, cxxvi., No 25, June 20, 1898.

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* An experiment in which one of the joints of the couple, already cooled in liquid oxygen, was lowered into ozone already liquefied and kept at 184·4°, was interrupted by a violent explosion.

† I was helped very considerably in these experiments by one of my old pupils, M. Lamotte, now at the Sorbonne.

A METHOD OF ESTIMATING NITRITES IN WATER.

By LUCIEN ROBIN.

This process is based on the fact that when we add pure iodide of potassium to a solution of a nitrite, then a little acetic acid, and let it stand for some time, the quantity of iodine set at liberty is always the same for a given quantity of nitrous acid, if we take care that the conditions of the experiment are always identical. The free iodide is estimated by means of a weak solution of hyposulphite of soda.

The method of working is as follows:—

If the water is not clear, it is necessary to filter it; if it is much coloured, sulphate of alumina and carbonate of soda must be successively added to it, as in the metaphenyldiamine method, in which we measure 100 c.c., to which are added 2 c.c. of glacial acetic acid; we then collect 50 c.c. of this solution by distillation.

Finally, if the water contains sulphuretted hydrogen, we treat 125 c.c. with a solution of sulphate of silver, then—after having filtered 100 c.c.—distil as above.

But in any case we add to 50 c.c. of the water under examination 2 c.c. of a chemically pure solution of iodide of potassium at 20 per cent; then, after shaking well, 2 c.c. of glacial acetic acid; shake again, and allow to stand for exactly half an hour; after having added a small quantity of starch solution, we determine the free iodine by means of a weak solution of pure hyposulphite of soda, prepared by diluting down 50 c.c. of the decinormal solution (24·764 grms. per litre) to 1 litre. We then look in the table below for the quantity of free nitrous acid per litre, according to the quantity of hyposulphite used. If the tint then becomes of a yellowish brown, it is necessary first of all to dilute the original sample of water. On the other hand, it is necessary to make quite sure that the iodide used is quite free from iodate, by making a blank experiment with it.

We can by this means recognise and estimate 0·005 m.grm. of nitrous acid in 50 c.c. of water,—that is to say, 0·1 grm. per litre.

The sensitiveness of this method is very great, and superior to that of the metaphenylene-diamine method. On a large number of experiments that I have made the greatest difference has been 0·3 m.grm. per litre, and that with waters of very diverse characters.

Table giving in m.grms. per litre the quantity of nitrous acid contained in a litre of water, according to the number of c.c. of the solution of hyposulphite of soda used, the sample taken being 50 c.c.

Hyposulphite c.c. used. C.c.	Nitrous acid per litre. M.grm.	Hyposulphite c.c. used. C.c.	Nitrous acid per litre. M.grm.	Hyposulphite c.c. used. C.c.	Nitrous acid per litre. M.grm.	Hyposulphite c.c. used. C.c.	Nitrous acid per litre. M.grm.
0·4	0·1	7·3	1·1	13·3	2·1	16·4	3·1
0·9	0·2	8·0	1·2	13·7	2·2	16·5	3·2
1·4	0·3	8·8	1·3	14·2	2·3	16·6	3·3
2·1	0·4	9·6	1·4	14·4	2·4	16·8	3·4
2·7	0·5	10·5	1·5	14·9	2·5	17·0	3·5
3·5	0·6	11·1	1·6	15·2	2·6	17·3	3·6
4·3	0·7	11·6	1·7	15·5	2·7	17·4	3·7
4·9	0·8	11·9	1·8	15·8	2·8	17·5	3·8
5·9	0·9	12·2	1·9	16·0	2·9	17·6	3·9
6·6	1·0	12·7	2·0	16·3	3·0	17·7	4·0

The figures in this table have been established by using distilled water to which has been added nitrite of soda in increasing doses, and four estimations made on each sample; I then took the mean.

Note.—If for one reason or another we cannot do the titration with the hyposulphite immediately the half-hour is up, it will be necessary to stop the decomposing action of the acetic acid on the nitrites, and thus the liberation of iodine, by adding 10 c.c. of a concentrated solution of pure carbonate of potassium.—*Journ. de Pharm. et de Chim.*, Series 6, vol. vii., No. 12, June 15, 1898.

ON THE ACTION OF SOME CARBONATES ON CHROMOUS ACETATE.

By G. BAUGÉ.

In a paper entitled "On a Crystallised Ammoniacal Chromous Carbonate," published in the *Comptes Rendus* (vol. cxxii., p. 474), we showed that if an aqueous solution of an alkaline carbonate was treated with chromous acetate, a double carbonate of protoxide of chromium and the alkali was formed; we have since been able to prepare, by the same method, a double carbonate of protoxide of chromium and sodium (*Comptes Rendus*, cxxv., p. 1177.

We have now examined the action of carbonate of potassium, carbonate of magnesium, and the carbonates the alkaline earths on chromous acetate.

Some time ago, M. Henri Sainte-Claire Deville (*Ann. de Chem. et de Phys.*, Series 3, vol. xxxiii., p. 75) pointed out that by reacting with a solution of bicarbonate, sesquicarbonate, or an alkaline neutral carbonate, on a soluble metallic salt, we could prepare double carbonates.

Action of Carbonate of Potassium. — Carbonate of potassium forms two compounds with chromous carbonate, one yellow, the other a reddish brown.

Preparation of the Yellow Salt.—A current of carbonic acid is brought into the tubulated flask of the apparatus already described (*loc. cit.*), then a certain quantity of chromous acetate suspended in water is introduced. After standing, the limpid solution is decanted and replaced by a solution of one-fifth the strength of carbonate of potassium in boiled water. On agitating the chromous acetate is dissolved, and a yellow crystalline powder is then precipitated. The above degree of concentration is important to notice, for in the case of liquids richer in carbonate of potassium the salt is decomposed too slowly, and when the solution is weaker it remains completely dissolved.

After decanting the mother-liquors, we wash the product first with cold boiled water, using as small a quantity as possible, until the wash-waters do not contain any more acetate of potassium; then with alcohol at 98°, and this is continued until the alcohol leaves the apparatus at the same strength at which it enters. After a final decantation the product is dried in the same flask, by placing it over a water-bath containing water boiling freely.

The compound can also be prepared by acting on the moist acetate with a warm saturated solution of bicarbonate of potassium. In this case a strong effervescence takes place, due to the giving off of half the carbonic acid.

Properties. — This salt is a powder having a yellow colour very similar to that of ferrous oxalate. Under the microscope it appears under the form of citron-yellow hexagonal prisms. It is soluble in water, which it colours a yellowish brown.

Solutions thus obtained gradually deposit the salts they contain, and at the same time lose their colour. If we attempt to take up the deposited salt with boiled water, we observe that its solubility is much diminished, and may even become *nil* after a few months.

Independently of this polymerisation, certain agents—and in particular carbonate of potassium—added to the solution of this salt will cause a partial, or even total, precipitation if the addition is sufficient.

Like the corresponding compounds of ammonium and sodium, it is an energetic reducing agent. It decomposes water below the boiling-point. When heated *in vacuo*, or in a current of inert gas, it has the property—like the corresponding yellow salt of sodium—of becoming brown, then regaining its original colour on cooling: this phenomenon takes place up to 280°, at which temperature it decomposes.

Chlorine and sulphuretted hydrogen attack it when warm, giving the same reactions as the yellow salt of sodium.

Though stable for some time in dry air, it quickly oxidises in moist air with the formation of a hydrated sesquioxide of chromium.

Heated in air, it gives the corresponding chromate.

Finally, dilute acids dissolve it when kept from the air, giving blue solutions.

Analysis.—When calcined in a current of dry air, and deprived of carbonic acid, this salt gives us water and carbonic acid. In the chromate of potassium which forms the residue, the chromium was determined in the state of oxide after precipitation by mercurous nitrate; then the potash was estimated in the form of sulphate after eliminating the mercury by means of sulphuretted hydrogen. The following results were obtained:—

	I.	II.	Theory.
CO_2	31·70	31·92	31·76
K	28·01	27·98	28·15
Cr	18·76	18·89	18·77
H_2O	9·70	9·91	9·74

The red salt of which we have already spoken is prepared by placing the yellow salt in boiled water, and passing a current of carbonic acid for a prolonged period. The yellow salt becomes gradually transformed into a brick-red compound. This transformation is also effected in alcohol at 60°. Unfortunately the attack is only superficial, and the product of the reaction has not a constant composition. This red substance can be prepared directly by acting on moist chromous acetate with a 1/30th solution of carbonate of potassium in the exact quantity necessary. In this case a red precipitate is formed which is partially destroyed by washing, and of which the analysis could not be made.

This salt, like the preceding one, decomposes water at 100°.

Action of Carbonate of Magnesium.—If we place a moist solution of chromous acetate in contact with a saturated solution of hydrocarbonate of magnesium, in water charged with carbonic acid, a reaction takes place with the formation of a brownish red body which decomposes water on boiling. We have not been able to make the analysis, for at the same time that the double salt is precipitated there is a deposit of carbonate of magnesium, which we have not been able to separate in a satisfactory manner.

We have not succeeded in obtaining double compounds with the alkaline earthy carbonates.

To sum up, chromous carbonate forms with carbonate of potassium a double salt of a yellow colour, in sharp well-defined crystals, to which analysis gives the formula $(CO_3K_2,CO_3Cr)_2 3H_2O$, and a crystallised double salt of a reddish colour with an undetermined formula. Carbonate of magnesium combines with chromous carbonate, giving a reddish brown compound.

The alkaline earthy carbonates are without action.—*Comptes Rendus*, cxxvi., No. 22, May 31, 1898.

SOLUTIONS OF SILICATES OF THE ALKALIES.*

By LOUIS KAHLENBERG and AZARIAH T. LINCOLN.

Introduction.

The electrical conductivity of solutions of sodium silicates has been investigated by F. Kohlrausch (*Zeit. Phys. Chem.*, xii., 773, 1893), who worked mainly with the compounds corresponding to the formulæ Na_2SiO_3 and $Na_2O.3.4SiO_2$, although he also tested the conductivity of solutions containing sodium hydroxide and silicic acid in other proportions varying from pure NaOH to the acid silicate just mentioned. Kohlrausch obtained the solution of the normal silicate by dissolving the crystallised salt ($Na_2SiO_3 + 9H_2O$) in water, while that of the acid silicate was prepared by boiling the solution of the normal salt with excess of silicic acid. By mixing sodium hydroxide with various quantities of the acid silicate, the other solutions mentioned were obtained. Kohlrausch found that a dilute solution of sodium silicate conducts electricity better than that of any other salt of equivalent concentration, and concludes that this is due to the fact that in solution this salt suffers hydrolytic decomposition into sodium hydroxide and silicic acid. In concentrated solutions Na_2SiO_3 was found to be a rather poor conductor. Dilute solutions of the acid silicate were also found to conduct well, while strong solutions showed an abnormally low conductivity. This behaviour is also explained by the hydrolytic decomposition of the salt. Kohlrausch (see paragraph 2, p. 773; also p. 778, *loc. cit.*), appears to give this explanation in rather a tentative way, for, besides the fact that silicate solutions have an alkaline reaction and that the alkali they contain can be estimated by titrating with a normal acid, he had simply the results of conductivity determinations upon which to base his argument. No doubt the high conductivity of a solution of Na_2SiO_3, which, if the salt were supposed to dissociate into the ions 2Na and SiO_3, would necessitate the assumption that the latter ion has a mobility exceeding that of the chlorine ion by about 70 per cent, is an excellent reason for believing that the silicate is decomposed into NaOH and silicic acid, and that the great conductivity of the solution is due to the presence of the mobile ion OH; nevertheless a determination of the freezing-points of solutions of silicates together with conductivity investigations, would more definitely answer the question as to whether these compounds are hydrolytically decomposed, and would furthermore enable one to make a quantitative estimate of the extent of such decomposition. To determine the extent of the hydrolytic decomposition of the silicate from the electrical conductivity of its solution is not possible, for the silicic acid split off exercises an unknown retarding influence on the movements of the ions. It is possible only to state, as Kohlrausch does, that in very dilute solutions the decomposition is very great and that probably even in strong solutions it is still appreciable. Colloidal silicic acid has but very little effect on the freezing point, as is well known; indeed, in the case of a solution of sodium silicate the lowering of the freezing-point caused by the colloidal silicic acid present is generally so small that for most purposes it may be left out of consideration. From this it is evident that from the lowering of the freezing-point of a silicate solution the extent of the hydrolytic decomposition of the salt may be calculated very approximately. The present investigation was undertaken in order to throw more light on the nature of silicates in solution; for this purpose the freezing-points and the electrical conductivity of solutions of various silicates were determined.

Experimental Part.

The solutions that were investigated are those of the silicates of sodium, potassium, lithium, rubidium, and cæsium. These solutions were in all cases prepared by adding to a solution of silicic acid, obtained by dialysis according to the well-known method of Graham (*Phil. Trans. Roy. Soc.*, London, 1861), the required amount of a standard solution of the pure hydroxide of the alkali metal. That a solution of sodium silicate thus prepared is the same as that obtained by dissolving the salt will be shown below. It is a well established fact that a solution of NaCl is the same as that obtained by mixing equivalent quantities of NaOH and HCl (*Ostwald, Zeit. Phys. Chem.*, 2, 80, 1888), and consequently it seemed at first unnecessary to prove that a solution of Na_2SiO_3 is the same as a solution of equivalent amounts of silicate acid and caustic soda; but because in the case of silicate solutions equilibrium is established only after a measurable period of time (*Kohlrausch, loc. cit*, p. 783), and because objections might possibly arise to using a colloidal solution of silicic acid in the preparation of silicate solutions and then finding that the latter contain colloidal silicic acid, it was thought best not to omit the experimental proof.

Dialysed solutions of silicic acid were prepared, using crystallised $Na_2SiO_3 + 9H_2O$ and also commercial solutions of water-glass from different manufacturers. In each case the dialysis was carried on until no more chlorides were present in the solutions. No difference was found in the behaviour of the solutions of the silicates prepared from the various colloidal silicic acid solutions thus obtained. The strength of the silicic acid solutions was determined by evaporating a measured quantity to dryness, igniting and weighing the SiO_2; the purity of the latter was always established by finally volatilising the same with hydrofluoric acid—no residue remained.

The solutions of the hydroxides of sodium and potassium were obtained by allowing the metals to act upon water freed from carbon dioxide. The hydroxides of lithium, rubidium, and cæsium were prepared by treating the sulphates of these metals with equivalent amounts of barium hydroxide. The strength of the solutions of these alkaline hydroxides was determined by comparison with a carefully standardised solution of hydrochloric acid.

The freezing-point determinations were made with the apparatus of Beckmann. The thermometer was graduated to hundredths of a degree and admitted of judging the thousandths by use of a lens. The usual precautions (see Ostwald's "Hand. u. Hilfsbuch." in making the freezing-point determinations were carefully observed.

The electrical conductivity was measured according to the method of Kohlrausch. In preparing the various solutions, water carefully freed from carbon dioxide and ammonium salts was used. The water was first distilled from potassium bichromate plus sulphuric acid and then re-distilled from barium hydroxide. A condenser of block tin was used; this was found to yield satisfactory results. The water thus obtained was carefully protected from the carbon dioxide of the air, and special precautions were taken in carrying out all the experiments to exclude the influence of carbon dioxide.

In preparing the silicate solutions the aim was to get fairly strong solutions with which to begin. In attempting this by the method of mixing caustic alkali with colloidal silicic acid some difficulty was encountered. The advantage of using this method of getting the solutions of the various silicates is clearly that, by means of it, it is possible to more conveniently get the alkali and the silicic acid into solution in any desired proportions. The disadvantage is that very strong solutions cannot be thus prepared, for the reason that, when strong solutions of caustic alkali and silicic acid are mixed, the latter gelatinises. Various attempts to get a solution of the normal silicates of sodium or potassium stronger than one-eighth of a grm.-molecule per litre failed because the solutions gelatinised before the proper amount of alkali had been added. Still more difficulty was encountered in preparing the solution of the normal silicate of lithium. In this case a solution containing one thirty-second of a

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* *Journal of Physical Chemistry*, vol. ii., No. 2, February, p. 77 (1898).

grm.-molecule per litre was the strongest that could readily be obtained. In mixing the alkali with the silicic acid solution, it was found best to add the former to the latter gradually, always shaking the mixture and waiting until the precipitate that forms temporarily is completely dissolved before adding more alkali. It is best also to heat the silicic acid solution while the alkali is being added. The colloidal solution of silicic acid was slightly opalescent in appearance; the solutions of the silicates, however, were invariably perfectly clear.

Tables I. to IX. give the results of the cryoscopic determinations. In the first column, under *v*. is given the volume in litres in which one grm.-molecule of the salt expressed by the formula is contained. The second column gives the observed lowering of the freezing-point. In the third column are the molecular weights calculated on the supposition that the salt when in solution has the composition indicated by the formula. The fourth column gives the molecular weights calculated on the supposition that there is in the solution only the alkaline hydroxide; that is to say, in this calculation no account was taken of the silicic acid present. The solution of silicic acid that was used in preparing the silicate solutions according to the method above described contained 12·2180 grms. SiO_2 per litre and had a freezing-point of −0·018, which corresponds to the molecular weight 1019.

The first part of Table I. gives the results obtained from freezing solutions of Na_2SiO_3 prepared by mixing solutions of silicic acid with caustic soda as above described; the second part gives the results obtained from freezing solutions of Na_2SiO_3 prepared by dissolving the salt obtained by fusing the alkali and the acid together. It will be observed that the freezing-points of the corresponding dilutions agree fairly well, and justify the conclusion that the solutions are identical. The fact that the depressions in the second series are not quite as large as those in the first, is very likely due to the slight formation of carbonates in case of the salt obtained by fusion, for in the process of fusing it is especially difficult to exclude the influence of carbon dioxide. Tests of the electrical conductivity of the solutions obtained in these two different ways also pointed to the fact that they are identical. The salt obtained by fusion of course had a slightly lower conductivity for the same reason that its solution possessed a slightly higher freezing-point.

Table I. shows that the molecular weights calculated on the assumption that the substance in solution has the formula Na_2SiO_3 approach as their limit the value of one-fourth the calculated molecular weight of Na_2SiO_3. There are then in the dilute solutions four part-molecules active in lowering the freezing-point. The action of water on the silicate may be expressed by the equation—

$$Na_2SiO_3 + \text{water} = 2\overset{+}{Na}, \overset{-}{OH} + \text{colloidal silicic acid.}$$

The four part-molecules that are active in lowering the freezing-points are thus two sodium ions and two hydroxyl ions. As stated above, the effect of the colloidal silicic acid on the freezing-point can—at least for the more dilute solutions investigated—be considered too small to take into account. The results show that this hydrolytic decomposition is nearly complete for the concentration $v=48$, and that it has progressed to the extent of 64·8 per cent* even when $v=8$. The last column of the table giving the molecular weights calculated on the assumption that there is only NaOH in the solution, confirms in a striking manner what has just been said. These results approach as their limiting value one-half the molecular weight of NaOH. This is what would be expected, since this compound dissociates into the ions Na and OH.

The investigations of solutions containing $NaHSiO_3$ yielded the results in Table II. Here the molecular weights calculated from the observed lowerings on the

TABLE I.

Na_2SiO_3. Molecular Weight = 121·58.

v.	Freezing-point.	Mol. wt.	Mol. wt. (NaOH).
8	0·695	41·3	27·0
12	0·498	38·4	25·2
16	0·385	37·3	24·4
24	0·280	34·2	23·9
32	0·210	34·9	22·4
48	0·150	31·9	20·9
64	0·110	32·6	21·4

¼ of 121·58=30·39. ½ Mol. wt. NaOH=19·88.

Na_2SiO_3 (obtained by Fusion).

v.	Freezing-point.	Mol. wt.
32	0·200	36·5
48	0·140	34·8
64	0·108	33·8
96	0·077	31·6

TABLE II.

$NaHSiO_3$. Molecular Weight = 99·7.

v.	Freezing-point.	Mol. wt.	Mol. wt. (NaOH).
8	0·332	70·9	31·0
12	0·263	59·7	26·1
16	0·202	58·3	25·5
24	0·146	53·7	23·5
32	0·110	53·5	23·4

½ of 99·7=49·85.

TABLE III.

$Na_2Si_5O_{11}$. Molecular Weight = 361·34.

v.	Freezing-point.	Mol. wt.	Mol. wt. (NaOH).
32	0·178	119·9	27·0
48	0·139	102·4	23·1
64	0·104	100·3	22·6
96	0·089	79·9	18·0
128	0·059	90·4	20·4

¼ of 361·34=90·33.

TABLE IV.

K_2SiO_3. Molecular Weight = 153·46.

v.	Freezing-point.	Mol. wt.	Mol. wt. (KOH).
8	0·710	51·1	37·1
12	0·503	48·1	34·9
16	0·394	45·4	32·9
24	0·279	43·5	31·4
32	0·215	42·2	30·6
48	0·146	41·4	30·0
64	0·110	41·2	29·9
96	0·082	36·8	26·7

¼ of 153·46=38·36. ½ Mol. wt. KOH=27·85.

TABLE V.

$KHSiO_3$. Molecular Weight = 115·64.

v.	Freezing-point.	Mol. wt.	Mol. wt. (KOH).
8	0·326	83·8	40·4
12	0·248	73·4	35·4
16	0·196	69·7	33·6
24	0·153	59·5	28·7
32	0·110	62·1	29·9
48	0·078	58·4	28·1

½ of 115·64=57·82.

TABLE VI.

Li_2SiO_3. Molecular Weight = 89·76.

v.	Freezing-point.	Mol. wt.	Mol. wt. (LiOH).
32	0·228	23·3	12·4
48	0·166	21·2	11·3
64	0·120	22·1	10·4
96	0·090	19·6	10·4
128	0·071	18·5	9·9

¼ of 89·76=22·88. ½ Mol. wt. LiOH=11·92.

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* This calculation, as well as the similar ones that follow, has been made on the supposition that the caustic alkali present in the solution has suffered practically complete electrolytic dissociation.

assumption that the dissolved substance is $NaHSiO_3$ give values that approach as their limit one-half of the molecular weight of $NaHSiO_3$. This shows that in the dilute solutions there are two part-molecules active in lowering the freeeing-point; these are sodium and hydroxyl ions as before. The equation expressing the action of water on $NaHSiO_3$ may be written—

$$NaHSiO_3 + \text{water} = \overset{+}{Na}, \overset{-}{OH} + \text{colloidal silicic acid.}$$

This decomposition is nearly complete at the same concentration as that of Na_2SiO_3, and even when $v=8$ it has progressed to the extent of 40·7 per cent. As in the case of Table I., the values in the last column (obtained on the supposition that the solution is simply one of NaOH) approach the limit of one-half the molecular weight of NaOH.

Table III. gives the results obtained by freezing solutions of the more acid silicate $Na_2Si_5O_{11}$. This salt was selected because a lithium silicate of analogous formula occurs in Nature. The molecular weights in the third column approach as a limit the value of one-fourth the molecular weight of $Na_2Si_5O_{11}$.* Here again then there are four part-molecules active in lowering the freezing-point. The equation—

$$Na_2Si_5O_{11} + \text{water} = 2\overset{+}{Na}, \overset{-}{OH} + \text{colloidal silicic acid}$$

expresses the hydrolytic decomposition that takes place. This decomposition is practically complete at $v=128$, and has gone on to the extent of 67·3 per cent even when $v=32$. In the fourth column the molecular weights, calculated on the basis that there is only NaOH in solution, again approach as a limit the value of one-half of the molecular weight of NaOH. This salt then behaves very much like those of Tables I. and II., except that the hydrolytic decomposition is not as far advanced at the same stage of dilution. This is to be expected from the law of mass action. For a like reason $NaHSiO_3$ is not quite as far dissociated hydrolytically at the same degree of dilution as Na_2SiO_3, though here the difference is less since the amount of silicic acid present has only been doubled, while in the salt $Na_2Si_5O_{11}$ there is five times as much acid (to the same amount of sodium) as is contained in the normal salt.

Tables IV. and V. show the behaviour of solutions of K_2SiO_3 and $KHSiO_3$ respectively. What has been said of the sodium compounds applies also to these salts. The action of water on these silicates may be expressed by analogous equations. At $v=8$ the normal salt is dissociated 66·9 per cent and the acid salt 39 per cent. In both cases the dissociation is practically complete at $v=48$.

(To be continued).

NOTICES OF BOOKS.

A Laboratory Guide in Qualitative Chemical Analysis. By Horace L. Wells, Professor of Analytical Chemistry and Metallurgy in the Sheffield Scientific School of Yale University. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1898. Pp. vii.—189. 8vo.

A Short Course in Inorganic Qualitative Analysis. (For Engineering Students). By J. S. C. Wells, Instructor in Analytical Chemistry, Columbia University. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1898. Pp. vii.—294. 12mo.

These two works covering practically the same field, published simultaneously by a well-known New York firm, and written by teachers of experience in universities less than 75 miles apart, are quite unlike as respects the methods of treatment and their educational influence. Both admit the value of the classical work of Fresenius and recommend it for reference. Dr. Wells, of Columbia University, follows conservative methods of instruction; Professor Wells, of Yale University, adopts a novel plan for training students to think for themselves. In many ways the two books present marked contrasts; Professor Wells deprecates the use of "tables or abbreviated schemes of analysis," Dr. Wells depends largely on "Schemes," neatly printed on folding sheets for imparting instruction; Professor Wells takes up the study of the groups of radicals (metals) in an inverse order to that followed by Dr. Wells; the former teacher assumes that the students beginning the subject of qualitative analysis possess a good knowledge of elementary chemistry including the fundamental theories; the latter teacher finds it expedient to insert in his book brief paragraphs of descriptive chemistry containing elementary data. Dr. Wells obliges the student to spend much time in examining the individual reactions of the metals and acids, before considering their group relations; Professor Wells introduces the student at once to the behaviour of groups of metals having common reactions. Dr. Wells's method of instruction is adapted rather to drilling large classes of students. Professor Wells, on the other hand, aims to prevent mere mechanical work on the part of the students, and the use of his book pre-supposes close contact with the individual. In both books the subject-matter is clearly and ably presented, and it would be invidious to say that one was decidedly better than the other. A student working through either the "Guide" or the "Short Course" conscientiously, would acquire a good knowledge of qualitative analysis.

Professor Wells places before the beginner twenty-seven solutions in labelled bottles and by studying these with the standard reagents he is expected to become familiar with the behaviour of the metals singly and in groups. The solutions comprise salts of aluminium, ammonium, antimony, arsenic, barium, and so on, to strontium and zinc, all arranged alphabetically. The first exercise is to "find by experiment which of the twenty-seven solutions give precipitates when a few drops of HCl are added to 1 or 2 c.c. in a test tube." The student is then directed to write the equation of each reaction and to remember the facts observed. By this means he becomes acquainted with the Ag, Pb, Hg group. In a similar way the student is directed to make experiments which teach him the methods of recognising the three chlorides when mixed. Results of experiments are never given to the worker with test tube, who is supposed to observe, remember, and reflect. Instructions for ascertaining which of the twenty-seven solutions react with hydrogen sulphide then lead to an acquaintance with a second group, and so on. Part II. is devoted to "Theory," explaining chemical radicals, ionisation and ions, classification of radicals and salts and methods of writing chemical equations. Part III., "Descriptive Part," gives a brief account of the principle reactions of the inorganic radicals and serves as a vocabulary to a reading book in some foreign language. In this part there are constant references to Fresenius. In an appendix are printed in large type labels for the twenty-seven experimental solutions and for reagents both liquid and solid. The pages of labels are perforated to permit their being torn out without injury to the book. A full table of contents serves for an index. The author acknowledged the assistance of Miss L. P. Bush in proof-reading, but both of them overlooked a typographical error in the title on page 1, where qualitative appears as oualitative.

Dr. Wells's "Short Course" follows more closely the lines of Fresenius; the more important reactions of the different metals and acids are first explained, and the separation methods are given in schemes accompanied by notes, and in tables of schemes showing the reactions. These tables of schemes are an important feature of the

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* The small molecular weight found corresponding to the concentration $v=96$ is no doubt due to experimental error.

book for those students who take kindly to synoptical diagrams.

Neither of these works teach the student much of blowpipe analysis, as the subject is probably handled in another department or in another treatise, but the writer feels that it is of great advantage to unite the dry and wet methods in elementary instruction, the former often furnishing a quick and accurate means of recognising a substance.

Review and Bibliography of the Metallic Carbides. By J. A. Mathews. Smithsonian Miscellaneous Collections, No. 1090. City of Washington. 1898. 32 pp. 8vo.

Since the manufacture of acetylene gas from calcium carbide has become commercially profitable, the metallic Carbides have acquired new interest, and Mr. Mathews's "Review and Bibliography" will be welcomed by chemists and by firms engaged in industries in which these chemical compounds are used. The compiler's plan is a very good one; he gives a condensed account of the carbides in alphabetical order, and each is followed by references to literature bearing thereon. Moissan leads all other chemists in the number and importance of his contributions to the subject.

Mr. Mathews, writing in 1897, does not speak very hopefully of the future of acetylene gas for the purposes of illumination. In a postscript he gives the literature down to March, 1898. The booklet is published by the Smithsonian Institution on recommendation of the Committee on Indexing Chemical Literature appointed in 1882 by the American Association for the Advancement of Science. H. C. B.

CORRESPONDENCE.

THE NEW GASES.

To the Editor of the Chemical News.

Sir,—I fear Mr. Richmond must be left to struggle with "the inadequacy of language to express ideas," since life is too short to follow him in his rambles through the dictionary. But to assist his ideas I will re-state the case as simply as possible.

Cavendish proved that when oxygen, nitrogen, and carbonic acid have been removed from air, a residue remains of unknown composition.

Lord Rayleigh proved that this residue is denser than nitrogen. Wishing to know a little more about the matter, and learning from Professor Dewar what it was that he had done, Lord Rayleigh was proceeding to collect a quantity of this residual gas for experiment when Professor Ramsay appeared upon the scene as a rival collector, and associated himself. Thenceforward the investigation was carried on by the two men jointly, and after a certain time they informed the world that the Cavendish residue is a hitherto unnoticed element, to which they gave the name of argon.

The world was very pleased, and then a little sceptical. The discoverers could not find that their element had a single chemical affinity, and its spectrum was a little peculiar. But they fought for it manfully, explained away its spectroscopic oddities, determined its constants, and all that sort of thing, and finally got the world to acquiesce —perhaps rather languidly—in their discovery.

Things were in this comparatively happy state when argon was suddenly dethroned, and by Professor Ramsay himself. He announced that what had been called argon and an element is two things, one of which he calls krypton, while the other may conveniently retain the original name. Some people were delighted, while others shrugged their shoulders, said they had expected it, and wondered when finality was to be reached. Sure enough the little stranger had scarcely got through its christening when it and argon were further split up to make four new elements by a fissiparous division better known in physiology than in physics. Neon and metargon are the two newest claimants for a place in Mendeleeff's table, but, like argon and krypton, they are known only as the unknown cause of certain lines in the spectrum.

It is a curious thing that, when neon and metargon were discovered, krypton modestly retired into its crypt. The quantity of "argon"—*i.e.*, of Cavendish residue—operated upon represented about the same quantity of air as that employed when krypton was found; yet there was no krypton, and the explanation of its absence did no particular credit to Professor Ramsay's ingenuity. Again, the spectrum which is the sole proof of the existence of metargon can unfortunately be produced by carbonic acid and cyanogen. Still more singular, the characteristic line which proves neon in London, proves metargon in Paris; and that same line D_5, as pointed out last week by "Puzzled," is indifferently produced by a gas having a density of 14·67 and by one of the density 19·87. If neon be spectroscopically equal to metargon, and metargon be equal to carbon compounds, and we don't know anything whatever about either of them except spectroscopically, and if a difference of density of 35 per cent does n't matter a pin, and if neither is found in the common matrix when krypton is discovered, and if krypton vanishes when they are discovered, then, Sir, I want to know—where are we?

I shall be pleased at any time to discuss the ethical standpoint of a gentleman who has posed in *Nature* as an expert on scientific morality. But just at present it is his science, not his morality, that is in question, and our poor language is surely not so hopelessly inadequate as to compel Mr. Richmond to mix up things so distinct. My point is that these unintelligible and contradictory results are not Science, but mere fumbling with Science; and that all we know at this moment about the Cavendish residue beyond what Cavendish knew, is that it is heavier than nitrogen, and is probably a mixture of unknown substances in unknown proportions. Not one of these substances so hurriedly announced by Professor Ramsay has been truly isolated or identified, or scientifically demonstrated in any way. That there are lines in the spectrum of air which do not belong to any demonstrated or accepted element was pointed out by other observers before Professor Ramsay. Will Mr. Richmond kindly point out what is the net addition to precise and positive knowledge that accrues to the world from this extraordinary jumble of argon, krypton, neon, and metargon?—I am, &c.,

Suum Cuique.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvi., No. 20, May 16, 1898.

Some Causes of Uncertainty in the Exact Estimation of Small Quantities of Carbonic Acid and Moisture in Large Volumes of Air or of Inert Gases. —A. Gautier.—A long paper, not suitable for abstraction.

Liquefaction of Hydrogen and Helium.—J. Dewar.—Already noticed.

On a Crookes Tube Regenerable by Osmose.—P. Villard.—To overcome the principal defects of a Crookes tube when employed for the production of X rays, viz., the increase or decrease of resistance, the author proposes the addition of a platinum tube closed at one end and with the open end sealed to a glass tube, itself sealed to the bulb. If, now, the platinum tube is heated by means of a Bunsen burner the conditions suggested by MM. Ste.-Claire Deville and Troost are realised. The hydrogen of the flame penetrates the platinum by osmose in a nearly pure state, and thus reaches the interior of the apparatus. The introduction of gas ceases as soon as the flame is withdrawn. If, now, the platinum tube is covered with a platinum sheath, so that the flame does not come in contact with it, but allowing free circulation of the air, and is then heated afresh, the gas previously introduced will now leave the apparatus, still by osmose, and a more perfect vacuum can be thus established. These two operations may be repeated as often as is desired.

On a Property of Fluorescent Screens.—P. Villard.—If a body opaque to X rays be placed between a Crookes tube and a platinocyanide of barium screen, so that the shadow of the obstacle is visible, it will be noticed that when the obstacle is removed and the X rays are allowed to fall on the whole surface of the screen, that part which was previously dark will now appear brighter than the rest; the difference being the more marked in proportion as the obstacle was more opaque.

Atomic Weights of Easily Liquefied Gases.—D. Berthelot.—A mathematical paper, not suitable for abstraction.

Preparation and Properties of Anhydrous Fluoride of Glucinum and of Oxyfluoride of Glucinum.—P. Lebeau.—This paper has already been inserted in full.

Synthetic Method of Forming Carbonylferrocyanide of Potassium.—J. A. Muller.—The author has recently succeeded in forming carbonylferrocyanide of potassium in a very simple manner by heating a solution of ordinary prussiate of potash in an atmosphere of carbonic oxide. If a solution of ferrocyanide of potassium at 200 grms. per litre is left in a closed vessel at the ordinary temperature (15° to 20°) in the presence of a quantity of carbonic oxide, a little more than equi-molecular, after the lapse of twelve hours no appreciable trace of carbonylferrocyanide is formed. After thirty days, $\frac{1}{4}$ per cent of the prussiate used is transformed into carbonylferrocyanide. At 60—65°, the quantity formed is 4 per cent in the same time; at 100° it is greater, and the reaction is much more rapid; and at 130°, it is more than 90 per cent. The reaction is complete in forty-eight hours. Ammonia and formate of potassium are also formed. The reaction may be expressed as follows:—

$$K_4Fe\bar{C}N_6 + CO + 2H_2O = K_3Fe\bar{C}N_3CO + NH_3 + HCO_2K.$$

New Incomplete Tertiary Alcohol, Dimethylheptenol.—Ph. Barbier.—The new unsaturated tertiary alcohol described in this paper is derived from lemonol by the action of alcoholic potash. A mixture of 200 grms. of lemonol and 100 grms. of potash dissolved in a very little alcohol is heated for eight hours at 150°. It is then precipitated by water, and the oily layer which separates is washed with a dilute solution of acetic acid, then with water, after which it is dried. The liquid obtained after two rectifications *in vacuo* gives a substance boiling at 79° at 10 m.m. It gives on analysis:—

	Found.	Calculated for $C_9H_{18}O$.
C	76·08	76·06
H	12·60	12·68

It is a colourless mobile liquid, with an odour recalling that of natural methylheptenone. It fixes one molecule of bromine, and when heated to 140° with acetic anhydride and a little melted acetate of sodium it gives an acetic ether boiling at 84—86° at 11 m.m. This liquid has an agreeable aromatic odour. The substance obtained under the above-mentioned conditions is, therefore, a non-saturated alcohol of the formula $C_9H_{18}O$, differing from the parent alcohol by having one atom of carbon less. The author has determined its constitution by the study of its products of oxidation.

Ethane-pyrocatechin and its Derivatives.—Ch. Moureu.—Ethane-pyrocatechin has already been prepared by Vorlander by heating pyrocatechin with potash, bromide of ethylene, and a little water at 100° in sealed tubes. The author has easily prepared large quantities by heating the mixture in a large flask filled with hydrogen and fitted with a vertical condenser. The product is an oil, insoluble in water, distilling at 216°, with a density of 1·186 at 0°. Permanganate of potash hardly attacks it. Chromic acid in acetic solution completely destroys the molecule, with the formation of oxalic and carbonic acids, without it being possible to isolate any intermediate body of a neutral, quinonic, or acid nature. Ethane-pyrocatechin behaves like an ordinary di-alcoholic ether of orthodiphenol, and the influence on the aromatic nucleus of the ethylenic ether function, which forms the oxygenated nucleus in itself, is analogous to that of two ether oxide functions with the chain open.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xix.-xx., No. 6.

On some Phenomena of Transposition, produced by Means of Hydriodic Acid at a high Temperature.—G. Blanc.—Hydriodic acid is a very powerful reducing agent, frequently used in the transformation of ketones, alcohols, amines, &c., &c. But it has other stronger properties, cited by the author; for instance, when fuming hydriodic acid is heated up to 200° in sealed tubes in the presence of carbide derivatives of the halogens, one obtains, not only the corresponding carbide, but also another product of molecular transposition. In some few cases the second is the only one present in the products of the reaction.

Combinations of Chromic and Titanic Acids.—M. Blondel.—Concentrated chromic acid will dissolve titanic acid. Under the most favourable conditions one equivalent of chromic will dissolve one equivalent of titanic acid. Such a solution is decomposed by progressive dilution, which precipitates products more and more rich in titanic acid. The compound richest in chromic acid is obtained in the state of an ammoniacal salt; the solution of one equivalent of titanic acid in four equivalents of CrO_3 and one equivalent of ammonia gives a precipitate of $2TiO_2,CrO_3,2H_2O$, while the mother liquor, evaporated in vacuo, deposits the salt $TiO_2,3CrO_3(NH_4)_2O,H_2O$ in hexagonal prisms.

On the Separation of the Oxides of Cerium and Thorium.—G. Wyrouboff and A. Verneuil.—Already inserted.

On the Yttric Earths Contained in the Monazite Sands.—P. Schutzenberger and O. Boudouard.—This article has already been inserted in full.

The Synthesis of Xanthic and Allied Bodies starting with Hydrocyanic Acid.—A. Gautier.—A short controversial article in which the author claims priority.

Action of Ammonia on Dithioacetylacetone.—V. Vaillant.—When a current of dry ammonia gas is passed through a solution of dithioacetylacetone in absolute ether at the ordinary temperature a voluminous pale yellow precipitate is obtained. This compound can also be obtained by treating an etherised solution of dithioacetylacetone by ammoniacal alcohol; the precipitate thus prepared is entirely crystalline, and is also much more stable than that obtained by the former method. The precipitate, after rapid filtration and washing with ether, is unstable, and at the ordinary temperature when exposed to air gives off ammonia, and returns to its previous state of dithioacetylacetone, but it can be kept for a long time in its original mother-liquor. The author has tried the same reaction on other compounds, with interesting results.

Thermic Study of the Acid Function of three Oxybenzoic Acids. Influence of Phenolic Oxyhydrile.—G. Massol.—The study of certain figures given by MM. Berthelot and Werner (*Ann. Chim. Phys.*, 6, vol. vii., pp. 146, 148, and 167) appears to show that the phenol function does not appear to exist in salicylic acid, while it is shown very clearly in the case of the meta- and para-isomers. The author decided to study the heat of formation of the three soda salts taken in the solid state. The influence of phenolic oxyhydrile notably stimulated the acid function of benzoic acid, and to determine the influence of alcoholic oxyhydride he took the heat of formation of meta- and para-oxybenzoates of soda. These results differed completely from those found when the acid was neutralised by the base in a weak solution.

The Separation and Estimation of Iodine, Bromine, and Chlorine.—Ad. Carnot.—Already inserted.

NOTES AND QUERIES.

⁂ Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Aniline Colours.—Where may I be able to find anything about the colouring power of the several aniline colours. I wish to colour 10 cubic metres of water, and I do not know which compound to use by preference.—K. Niuman, Valparaiso.

WORCESTERSHIRE COUNTY COUNCIL.

ADDITIONAL COUNTY ANALYST.

The SANITARY COMMITTEE of the WORCESTERSHIRE COUNTY COUNCIL are prepared to receive Applications from duly qualified persons for the Appointment of an additional County Analyst for the Administrative County of Worcester (exclusive of the County Boroughs of Worcester and Dudley) under the Sale of Food and Drugs Act, 1875, and the Fertilisers and Feeding Stuffs Act, 1893.

Salary £400 per annum, payable monthly, together with all necessary out-of-pocket expenses. Applications will only be received from persons between 25 and 40 years of age and capable of carrying out Bacteriological researches. A person qualified to lecture on Chemistry as applied to Agriculture will be preferred. The person appointed will, unless specially arranged to the contrary, have to devote his whole time to the service of the Council, and reside in or near Worcester. He must give security in such amount and of such nature as may from time to time be fixed and approved by the Finance Committee. He will be permitted, with the approval of the Sanitary Committee, to take a limited number of pupils, and must, if required, be prepared to lecture on and teach Analytical and Bacteriological work. He will also be required to do such Analytical and Bacteriological investigations as may be directed by the County Council.

The appointment will be held subject to six months notice on either side, which may be given at any time. No Superannuation or Pension will be paid. Office and Laboratory will be provided by the Council, together with all necessary Books, Stationery, Instruments, Chemicals, and other appliances. He will not be allowed to undertake private research work unless with the consent of the County Council.

The appointment will be subject to the approval of the Local Government Board and also of the Board of Agriculture.

Applications, stating the Candidate's age, where educated, present position, and previous experience (especially as to Analytical and Bacteriological work), must be made in the Applicants' own handwriting on paper of foolscap size, accompanied by not more than Six copies of recent testimonials, addressed to the undersigned and marked "County Analyst," so that it shall be received by 3 p.m. on Friday, the 19th day of August, 1898, and no application afterwards received will be entertained.

It is understood that the person appointed will also be appointed by the Corporation of Worcester to act as Analyst for the City of Worcester at an extra salary.

A printed statement of the duties may be obtained from me. Canvassing in any form will absolutely disqualify.

Selected Candidates will be required to attend a Meeting of the Sanitary Committee of the County Council, notice of which will be given.

The person appointed must be prepared to enter upon his duties not later than 1st October, 1898, and undergo a Medical Examination by an approved person.

S. THORNELY,
Clerk of the County Council.

Shire Hall, Worcester,
12th July, 1898.

The Sulphate of Ammonia Committee

OFFER

THE SUM OF 500 GUINEAS

To be given for the best Essay on the following subject:—

"THE UTILITY OF SULPHATE OF AMMONIA IN AGRICULTURE."

The subject to be treated from a practical and scientific point of view.

The Committee has secured the services of Mr. William C. Little, Member of the late Royal Commissions on Agriculture, and Dr. Voelcker, Consulting Chemist to the Royal Agricultural Society of England, to act as Judges of the Essays sent in. In the event of any difference arising, Mr. Samuel Rowlandson, a Member of the Council of the Royal Agricultural Society of England, will act as referee.

The Essays must be in the English language, and written on one side of the paper only; they must further bear a distinguishing motto or nom de plume, but not the names of the authors.

Each author, when sending in his Essay, must at the same time write his name and address on a slip, which he shall enclose in a separate envelope, seal the letter, and write outside it the motto or nom de plume he adopts for his Essay. The Essay and the envelope containing the slip to be sent in, under one cover, to the undersigned.

The envelopes containing the names of the authors will be opened in the presence of the Committee after the Judges have made their award.

All Essays must be in the hands of the undersigned not later than November 15th, 1898. The selected Essay will become the property of the Committee, who reserve to themselves the right to make such use of it as they may think fit.

The Committee also reserves to itself the right to purchase for a sum not exceeding fifty guineas any of the other Essays.

W. G. BLAGDEN (*Chairman*),
4, Fenchurch Avenue, London, E.C.

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WILLIAM F. CLAY, Bookseller, 18, Teviot Place, Edinburgh.

THE CHEMICAL NEWS.

Vol. LXXVIII., No. 2017.

PREPARATION OF CRYSTALLISED CALCIUM.

By HENRI MOISSAN.

Although calcium is very widely spread throughout nature, it has been impossible up to the present to obtain it pure in any notable quantity. The different methods used for its preparation have only enabled us to collect very small specimens, and its principal properties are far from being well known. Since the researches of Matthiessen it has been considered to be a yellow metal; we shall, however, show later on that it has the same colour as silver.

According to different workers who have been occupied with this subject, its density varies from 1·55 to 1·8. We must further remark that in the various papers treating of the subject of calcium, the authors have not given any analysis of the metal obtained. These several points serve to show the present state of the question.

Historical.

Experiments of Sir Humphry Davy.—The memorable experiment of Sir Humphry Davy on the decomposition of the alkaline earths by the electric current established the existence of a simple metallic body in lime. We know that by the decomposition of lime in the presence of mercury, or by the decomposition of a mixture of moist lime and mercuric oxide, he obtained an amalgam of calcium which decomposes water with great rapidity, re-forming slaked lime. The metal prepared by Sir Humphry Davy was white.

Matthiessen's Method.—By applying Bunsen's ideas (*Ann. der Chim. und Pharm.*, lxxxii., p. 137), Matthiessen (*Ibid.*, xciii., p. 277, 1855) succeeded in electrolysing a mixture of equal molecules of chloride of lime and chloride of strontium; under these conditions he obtained small metallic globules of a yellow colour. This experiment can easily be repeated, but it only gives very small returns; we have repeated it under the conditions laid down by Matthiessen, and also by increasing the size of the apparatus and the intensity of the current, but the returns were always of the smallest. The metal obtained certainly possesses a more or less pronounced yellow colour, resembling the colour of bell-metal.

Method of Liès-Bodart and Jobin.—In 1858 MM. Liès-Bodart and Jobin (*Ann. de Chim. et de Phys.*, Series 3, vol. liv., p. 363) described a chemical process for the production of calcium. They caused sodium to react on iodide of calcium in a state of fusion in an iron crucible closed with a screw-down cover. We repeated this experiment, but the results are very variable, as much from the point of view of the return obtained as to the purity of the product.

As a rule, by using 300 grms. of anhydrous iodide we can isolate a few metallic globules which together weigh about 6 to 8 grms. A certain proportion of the calcium is in the state of minute globules, distributed throughout the mass, and so small that they cannot be isolated.

Further, in some experiments, such as described by MM. Liès-Bodart and Jobin, we find globules of sodium not containing any calcium, as well as others of a yellow colour more or less rich in calcium, all mixed up together. If we analyse the metallic portions rich in calcium, we find that they contain very variable quantities of this metal. We obtained the following figures from the richest portions:—Ca per cent, 83·00, 88·30, 88·70, 93·20.

Temperature has a great influence on the returns.* If the reaction takes place at a dull red heat, the quantity of sodium contained in the metallic globules varies from 10 to 20 per cent, and the return is greater. If, on the contrary, the temperature is raised, and reaches a bright red, we obtain a metal containing a higher proportion of calcium, but the return is much lower.

Finally, when the heat is too great in the Liès-Bodart and Jobin method, we get no calcium at all; a new reaction takes place, to which we shall refer later on.

Sonstadt's Process.—Sonstadt (*Proc. Lit. and Phil. Soc. of Manchester*, 1864, p. 243) has applied the Liès-Bodart and Jobin reaction, by making the sodium react on a mixture of chloride of calcium and iodide of potassium. In this experiment we find, on the surface of the ingot of melted salts, a well melted, united metallic mass, which can be detached without any difficulty. This metal is brittle, with a crystalline texture, more often pyrophoric; it contains a notable quantity of the alkaline metals sodium and potassium. We repeated this operation four times, and the proportion of calcium in the metal never exceeded 20 per cent.

Caron's Method.—Caron (*Comptes Rendus*, vol. l., p. 547) has prepared calcium by reducing chloride of calcium by sodium in the presence of metallic zinc. An alloy of zinc and calcium is formed, which, when heated in a carbon crucible, leaves behind calcium which possesses the yellow colour of brass.

Winckler's Process.—M. Winckler (*D. Chem. G.*, vol. xxiii., pp. 44 and 120) first experimented on the reduction of lime by magnesium in a current of hydrogen gas; but he did not separate the calcium obtained from the magnesia. In a second paper (*D. Chem. G.*, xxiv., p. 1966) he deduced the formation, under the preceding conditions, of a hydride with the formula CaH, from the complex composition of the mixture remaining in the crucible; he did not, however, isolate any product.

To sum up, the difficulties met with in these different processes, and which prevent us obtaining calcium in a state of purity, are the following:—

1st. The separation of the calcium cannot be effected by the distillation of its amalgam; the residue is always impure.

2nd. By the electrolysis, by the dry method, of mixtures of salts of calcium and alkaline salts, it is the alkaline metal that is first set at liberty, and which then reacts more or less during electrolysis.

3rd. In the reduction by sodium there is always a mixture of sodium and calcium produced, since this latter metal, because of its reducing properties, acts in its turn on the salts present in the mixture. It forms an equilibrium varying according to the temperature and the bodies present in the reaction.

4th. Finally, whatever the method employed, it is impossible to distil the mercury or the excess of the alkaline metal in a current of hydrogen or of nitrogen.

With hydrogen the calcium produced rapidly forms, as we shall see later on, a perfectly white hydride with the formula CaH_2, and with nitrogen it forms a crystalline nitride. Hydrogen and nitrogen must therefore be absolutely kept away in all experiments on the preparation of calcium.

Preparation of Crystallised Calcium.—This preparation can be carried out by two distinct processes:—

1st. To obtain calcium in a state of purity we utilised the property this metal possesses (unknown up till now) of dissolving in liquid sodium kept at a dull red heat. On cooling, the calcium crystallises in the midst of the sodium, and by treating the metallic mass with absolute alcohol there remain brilliant white crystals of pure calcium of a hexagonal form.†

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* We repeated this experiment of MM. Liès-Bodart and Jobin ten times. In one operation we distilled the greater part of the sodium used, and we obtained a metallic ingot weighing 12 grms., containing 88 per cent of calcium.

† The calcium soluble in liquid sodium at a dull red heat is almost insoluble in this metal at its point of solidification.

The following is our method of working:—In an iron crucible of 1 litre capacity we place 600 grms. of crystallised anhydrous iodide of calcium and 240 grms. of sodium. The proportion of the alkaline metal present is three times as much as is required by the reaction—

$$CaI_2 + Na_2 = Ca + 2NaI.$$

The anhydrous crystallised iodide of calcium is roughly powdered, then mixed with pieces of sodium cut to about the size of a nut; the crucible is tightly closed by means of a screw-down cover, then kept for about an hour at a dull red heat. It is as well to agitate the crucible by a slight rotatory movement by means of a pair of tongs.

At the commencement of the operation a small quantity of the vapour of sodium escapes between the crucible and the lid; but, as the upper part gets heated less than the lower, as soon as the first disengagement of heat due to the reaction is finished, a little liquid sodium condenses in the thread of the screw, and the sealing of the joint is complete.

After cooling, the crucible is opened; it contains a layer of melted salt of a blue colour, surmounted by a metallic cake of sodium.

To separate the calcium we place about 500 c.c. of absolutely anhydrous alcohol in a flask of 1 litre capacity, kept cool by melting ice. The sodium taken from the crucible is thrown in in lumps of about 1 c.c. each. When all disengagement of hydrogen has ceased, we decant the liquid portion, and replace it with the same quantity of absolute alcohol.*

This washing is continued until the alcohol no longer leaves any fixed residue on evaporation. The brilliant powder remaining at the bottom of the flask is treated with anhydrous ether (previously kept over sodium), then placed in a glass tube, and dried at the ordinary temperature by a current of perfectly dry carbonic acid or hydrogen gas. The specimen should then be immediately sealed up in a glass tube.

It is necessary in all these operations to take the greatest precautions against the action of moisture and contact with air. This very finely divided crystalline powder oxidises with the greatest facility.

The return is about 50 per cent of the theoretical weight of the calcium used in the experiment. In our first experiments we obtained about 40 grms. of calcium at each operation.

2nd. We can also obtain calcium, either in crystals similar to those just described or in little melted globules, by means of the electrolysis of fused iodide of calcium at a dull red heat. This salt is a very good conductor of electricity. The negative electrode is of pure nickel, and the positive electrode—consisting of a cylinder of graphite—is placed in the axis of a porous pot. The temperature is maintained by the current at about the melting-point of iodide of calcium, which allows of the easy escape of the vapour of iodine. Under these conditions we obtain a white melted or crystalline metal. We are pursuing the study of this electrolysis.

Analysis.—To estimate the calcium in the metal prepared by the first process, we take a known weight and carefully decompose it by water. The hydrate of lime is dissolved in a few drops of nitric acid, the liquid is exactly neutralised with ammonia, and the calcium precipitated in the form of oxalate.

From the weight of quicklime obtained after filtration and calcination, the calcium is calculated. We obtained the following figures:—Calcium per cent, 98·9, 99·1, 99·2.
—*Comptes Rendus*, cxxvi., No. 25, June 20, 1898.

Heat of Formation of the Meta- and Para-oxybenzoates of Soda.—G. Massol.—These were determined by observing the heats of solution in water of the anhydrous neutral salts of soda, $C_7H_5O_3Na$; from these the heats of formation of the solid salts of soda, starting from the acid and the solid bases, were calculated.—*Bull. de la Soc. Chim. de Paris*, xix.-xx., No. 6.

ON THE PREPARATION AND PROPERTIES OF A NEW CARBIDE OF TUNGSTEN.

By P. WILLIAMS.

We have attempted to prepare double carbides of iron with a certain number of allied metals, such as chromium, molybdenum, tungsten, &c., and in examining the double compounds of tungsten and iron we have succeeded in isolating a new carbide of tungsten.

M. Moissan has described a compound (*Comptes Rendus*, cxxiii., p. 15) answering to the formula W_2C, which he obtained by heating tungsten with an excess of carbon in the electric furnace. This body is attacked by chlorine; but the new body is, on the contrary, clearly distinguished from this one, as chlorine has no action on it whatever. Its formula is WC. The present paper was written for the purpose of making known its preparation and principal properties.

Preparation of Carbide of Tungsten.

Carbide of tungsten, WC, may be obtained by one or other of the following methods:—

1. We make an intimate mixture of pure calcined tungstic acid, iron, and petroleum charcoal, in the following proportions:—

Tungstic acid	120 grms.
Charcoal	20 ,,
Iron	150 ,,

The mixture, placed in a carbon crucible, is heated to a reddish white heat by means of a powerful forge, for an hour. After cooling, we find a well melted button of iron at the bottom of the crucible; it is very hard and of a crystalline appearance. This button contains the carbide of tungsten mixed with a large quantity of iron and the double carbide.

To separate the carbide from the excess of iron, the button is attacked with warm hydrochloric acid until it is completely disintegrated. There remains a mixture of the double carbide of tungsten and iron, and of carbide of tungsten. We can separate the greater part of the simple carbide of the double compounds of iron and tungsten by means of a magnet, carbide of tungsten not being magnetic. This carbide is still mixed with graphite, but the great difference in the densities of the carbide and of graphite enable us to separate them very easily by levigation. The last traces of impurities are removed by a current of chlorine at a red heat. Finally, the use of bromoform or of iodide of methylene enables us to separate the small quantity of graphite which might have been liberated during the treatment with chlorine.

2. We can also prepare the carbide in the electric furnace. The same mixture, heated for five or six minutes with a current of 900 ampères and 45 volts will give a well melted button, easily broken, and also containing a good deal of graphite. The separation of the carbide is effected in the manner already described.

The crystals of the carbide prepared by the electric furnace are larger than those which we obtained by the use of the forge. The return is very small in either case; the carbide is found principally round the periphery of the button. We thought that this might be due to more rapid cooling; we therefore plunged the button, immediately on withdrawing it from the furnace, into a vessel filled with cold water, as described by M. Moissan in his experiments on the production of the diamond and of carbide of iron. In this manner we obtained a much greater yield, but the crystals were less well-defined.

Physical Properties.—Carbide of tungsten occurs in the form of an iron-grey powder; when examined under the microscope it is seen to be formed of non-transparent cubical crystals. It is very hard, and easily scratches quartz. The density at 18° is 15·7.

Carbide of tungsten melts with great difficulty. A small quantity was placed in a crucible of retort carbon

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* The alcohol has been first rid of air by boiling *in vacuo* at a low temperature, and then saturated with pure dry hydrogen gas.

and well closed; it was then heated for a quarter of an hour with a current of 950 ampères and 45 volts. The carbide WC was partially liquefied and transformed into W_2C and graphite, as shown by the analysis of the melted portion.

Chemical Properties.—Carbide of tungsten heated to a red heat in a current of pure dry hydrogen does not undergo any change. Heated in the presence of oxygen or of air it oxidises slowly, with the formation of tungstic and carbonic acids. Nitrogen is without action at a red heat.

Fluorine attacks it in the cold with incandescence, but chlorine, iodine, and bromine are entirely without action on the carbide even at a red heat. The gaseous hydracids and their solutions in water do not attack it. When heated with hydrochloric acid in a sealed tube for three hours, at a temperature of 350° C., there is no action between the carbide and the acid; but a considerable quantity of crystals of chloride of sodium separate out on cooling, on account of the glass having been attacked.

Nitric and sulphuric acids attack the carbide very slowly.

There is no action between water and carbide of tungsten up to the temperature of the softening of Bohemian glass. It is easily oxidised when heated with chlorate or nitrate of potassium; the bisulphate and the carbonate of potassium only attack it very slowly.

Analysis of Carbide of Tungsten.—The carbon is estimated by burning the carbide in a current of oxygen. The carbonic acid formed is absorbed in weighed potash tubes.

The tungsten is estimated by the oxidation of the carbide in a current of air; the tungstic acid thus formed is then weighed.

We have obtained the following figures:—

	I.	II.	III.	Calculated for WC.
Tungsten ..	93·55	93·52	93·60	93·88
Carbon ..	5·87	6·20	6·08	6·12

To sum up, we have prepared a carbide of tungsten of the formula WC. This carbide is formed when we heat a mixture of tungstic acid and carbon with a large excess of iron at the temperature of the electric furnace. In the presence of tungstic acid and carbon only, the carbide W_2C only is formed as described by M. Moissan.

Consequently, in the presence of carbide of iron, it is possible to obtain a compound of tungsten which contains twice as much carbon as that obtained by merely heating tungsten and carbon together. The iron, by facilitating the fusion of the mass, enables us to prepare this compound at a temperature lower than the fusing-point of tungsten, at which temperature the carbide WC only is formed.—*Comptes Rendus*, cxxvi., No. 24, June 13, 1898.

ON THE

ACTION OF SODAMMONIUM IN EXCESS ON RED PHOSPHORUS.

By C. HUGOT.

The results of the action of phosphorus in excess on sodammonium have already been published (*Comptes Rendus*, cxxi., p. 206). The action of sodammonium in excess on phosphorus gives rise to a compound the study of which is the object of this paper.

The apparatus used in these experiments consists of a tube containing recently melted soda, in which pure ammonia gas is liquefied. On contact with the sodic hydrate the liquid ammonia is completely dehydrated. The tube R, which serves as a reservoir for the ammonia gas, is closed by a glass tap. It is connected on the one hand with a mercury manometer, and on the other with the apparatus in which the reaction is to take place. On the small arm a tube is sealed, provided with a tap facilitating the collection over mercury of the gases disengaged during the experiment.

The apparatus in which the reaction of the phosphorus on the ammonium takes place is made entirely of glass. It is practically in the form of an H, of which the vertical sides are formed by the two tubes A and B, and the horizontal part by a narrow T tube plugged with dry glass wool.

The lower ends of the tubes A and B are drawn down fine, and for the weighings may be fitted with corks. The upper ends of A and B are both furnished with glass taps. It is by the tube A that the apparatus communicates with the reservoir of ammonia gas described above.

The following is the plan adopted for carrying out an experiment:—

The apparatus, A, T, B, carefully dried, is put in communication with the reservoir R. A current of ammonia gas traverses the apparatus, and completely drives out the air contained therein. The lower extremities are closed with corks, and the apparatus is weighed, full of ammonia.

We then introduce successively into the tube A a morsel of red phosphorus, well washed, and dried in a current of ammonia gas, and a globule of sodium, weighing the whole apparatus each time, full of ammonia gas as before. The sodium is introduced in the melted state in an atmosphere of pure dry hydrogen, after having been previously purified by distillation.

The weights of the phosphorus and the sodium being thus known, the lower extremities of the tubes A and B are sealed before the blowpipe. Communication is re-established between the reservoir and the apparatus which is plunged into a freezing mixture; sodammonium is formed, and dissolves in the excess of liquefied ammonia gas.

The phosphorus enters into reaction with the sodammonium. The liquid, which is at first of a reddish brown colour, slowly becomes greenish. This greenish tint is more or less bright, according to whether the phosphorus is present in greater or less proportion with regard to the sodium. We notice, at the same time, the formation of small brilliant crystals on the inner surface of the tube A.

During this operation, and especially after several hours' contact, hydrogen is given off, and may be collected over mercury.

After standing for a day, the apparatus being kept in melting ice, we caused the greenish liquid to pass from the tube A, through the glass wool, into the tube B, by inclining the apparatus. A large part of the excess of sodammonium passes over.

We then drive off the liquefied ammonia gas from B into A by distillation, by warming B and cooling A. We then run more liquid from A into B through the glass wool, or, in other words, we wash out the tube A with liquefied ammonia gas.

This operation should generally be repeated at intervals for several days, so as to remove the last traces of sodium, which suffice to colour the liquid a greenish blue. A crystalline powder of a yellow appearance remains in the tube A. If we allow these crystals to soak for some time in liquid ammonia, we notice that it takes a yellow tint. The washing of this crystalline powder can be carried out in the manner described above.

Still keeping the apparatus at 0°, the ammonia is gradually allowed to escape; there then remains a yellow deposit in B, which coats the inner surface of the tube, as well as crystalline sodium produced by the dissociation of the excess of sodammonium.

The yellow body contained in the tube B corresponds to the formula $P_2H_3Na_3$.

The crystals in the tube A, having a pale yellow colour, are crystals of amidide of sodium mixed with traces of the body $P_2H_3Na_3$.

If we analyse these crystals, after having washed them for several days in liquefied ammonia gas, we find that they correspond to the formula NH_2Na. The reaction which takes place in the tube may be represented by—

$$(a)\ 6NH_3Na+2P=P_2H_3Na_3+3NH_2Na+3NH_3.$$

The quantity of amidide of sodium formed is given by the weight of the crystals remaining in A. It is necessary to subtract the weight of the amidide formed by the spontaneous decomposition of the sodammonium noticed by M. Joannis (*Comptes Rendus*, cxii., p. 392). This quantity can be arrived at by estimating the hydrogen given off during the operation and collected over mercury. The yellow body, treated by acids and water, gives rise to the following reactions:—

$$(b)\ P_2H_3Na_3+3HCl=3NaCl+2PH_3.$$

$$(c)\ P_2H_3Na_3+3H_2O=3NaHO+2PH_3.$$

The phosphorus is deduced from the quantity of phosphide of hydrogen given off when we allow pure or slightly acidulated water to act slowly on the preceding body. The excess of sodium is known by the volume of hydrogen given off in these same reactions.

Heated *in vacuo*, the body $P_2H_3Na_3$, after having lost the small amount of ammonia gas it retained, gives off phosphide of hydrogen and a little hydrogen at about 100°. From 150° to 200°, on the contrary, the proportion of phosphide of hydrogen diminishes considerably; and, finally, at 200—300° the gas collected is only hydrogen.*

So as not to prolong these washings in liquid ammonia to too great an extent, it would appear, according to the formula (*a*) more convenient to cause the reaction between the sodium and the phosphorus to take place in proportions hardly higher than 3 to 1. Experience shows, however, that if we do not use a sufficient excess of sodium, the reaction (*a*) is not the only one that is produced. We have noticed the formation of compounds difficult to determine. We can, however, affirm the presence of the body PH_2Na to which M. Joannis (*Comptes Rendus*, cxix., 557) gave the name of phosphidide of sodium. — *Comptes Rendus*, cxxvi., No. 24.

NOTE ON LIQUID PHOSPHORUS.

By **F. P. VENABLE** and **A. W. BELDEN.**

In 1875 Hourton and Thompson (*Arch. de Pharm.*, 3, 6, 49), reported the formation of a peculiar modification of phosphorus formed on boiling ordinary phosphorus for five minutes with a strong solution of potash. The alkaline solution was poured off and the liquid phosphorus washed. It is said to remain liquid for months and solidifies only on cooling to +3·3°. It is further reported as not oxidising in the air nor giving off light in the dark. On becoming solid it forms ordinary wax-like phosphorus and a second variety of crystalline phosphorus.

These singular statements are cited in Dammer's "Handbuch der anorganischen Chemie," and the chemical literature available to us has been searched in vain for any further mention of this strange variety of phosphorus. It has, therefore, seemed advisable to give a brief notice of some experiments in which it was attempted to form this liquid phosphorus.

Five grms. of fresh wax phosphorus were placed in a flask with 80 c.c. of a saturated solution of potassium hydroxide and boiled for five minutes in a neutral atmosphere (nitrogen was used). This was washed with water at 19° and on the second washing the phosphorus solidified. If the alkaline solution was poured off directly, the phosphorus caught fire; hence it was usually poured off to small bulk, diluted with water, and again poured off, and so on, until the phosphorus was washed. In every experiment performed the phosphorus solidified after the second or third washing. The amount of phosphorus, the time of boiling (three, five, ten, and fifteen minutes), and the strength of the potassium hydroxide solution (saturated to 10 per cent solution), were each varied without securing the liquid phosphorus.

It is, however, true that the phosphorus becomes liquid on heating under the alkaline solution, and, if left covered with the same, stays liquid a long time, solidifying only when strongly cooled. It seems to give off occasional bubbles of gas during this standing and is probably being slowly changed into phosphine at ordinary temperatures. We are quite at a loss to know how the authors mentioned above secured their liquid phosphorus and how it could prove unalterable in the air. In all of our experiments it was peculiarly inflammable.—*Journal of the American Chemical Society*, vol. xx., No. 4.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JUNE 30TH, 1898.

By **SIR WILLIAM CROOKES, F.R.S.,**
and
PROFESSOR DEWAR, F.R.S.

To Major-General A. De Courcy Scott, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, July 11th, 1898.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from June 1st to June 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined by us, all were found to be clear, bright, and well filtered.

The rainfall at Oxford for the month of June is again considerably below the average; the actual fall being 1·34 inches; the thirty years' average is 2·11 inches, leaving a deficiency of 0·77 inch. This brings the deficiency for the first six months of this year to 3·34 inches.

Our bacteriological examinations of 252 samples have given the results recorded in the following table; we have also examined 39 other samples, from special wells, standpipes, &c., making a total of 291 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	390
New River, filtered (mean of 25 samples) ..	54
Thames, unfiltered (mean of 26 samples) ..	2321
Thames water, from the clear water wells of five Thames-derived supplies (mean of 124 samples)	57
Ditto ditto .. .. highest	2108
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 26 samples) ..	2149
River Lea, from the East London Company's clear water well (mean of 25 samples) . ..	33

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* The sum of the weights of the pure hydrogen and the hydrogen corresponding to the phosphide of hydrogen represents exactly the theoretical quantity of hydrogen contained in $P_2H_3Na_3$.

During the month the London waters have been of high dietetic quality. The number of microbes in the supply has been generally low, with the exception that on the 6th of June a sudden increase of harmless microbes took place in all the Companies' waters. The fact that this anomaly occurred simultaneously in all the filtered waters, suggests that it was due to some general cause, which at present remains unexplained.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

A METHOD FOR ESTIMATING PERCHLORATE IN NITRATES OF SODA AND POTASH.

By N. BLATTNER and J. BRASSEUR.

In their researches, carried out at Messrs. Kuhlmann's laboratory at Loos, on the presence and the influence of perchlorate in nitrates, MM. Blattner and Brasseur were led to search for a method of estimation which would be more simple and more exact than those already known. The following is what they have found:—

The chlorine in the chloride of sodium is first of all estimated in the ordinary way: 5 or 10 grms. of the nitrate under examination are then weighed while dry and finely pulverised; this is mixed with 8 or 15 grms. of pure lime, obtained by the calcination of pure precipitated carbonate of lime. The mixture is placed in a platinum or porcelain crucible, which must be covered and heated for fifteen minutes with a Bunsen burner. After cooling, the contents of the crucible are turned out into a flat-bottomed flask, and dissolved in dilute nitric acid free from chlorine.

In the solution the chlorine is estimated by nitrate of silver, either in acid solution according to Volhard's method, or in a solution neutralised by carbonate of lime, or by weighing the chloride of silver.

We thus obtain the chlorine in the chloride, the chlorate (if any is present), and in the perchlorate.

By difference with the first result, the proportion of perchlorate is calculated.

This method, which is simple and rapid, is at the same time perfectly exact. The following are a few results obtained with artificial mixtures of pure nitrates of soda and potash, with known varying proportions of perchlorate of potash:—

	Found.
Mixture with 1 per cent of perchlorate	1·010 per cent
,, 2 ,, ,,	2·026 — 2·012 ,,
,, 3 ,, ,,	3·015—3·006 ,,

—*Bull. Soc. Chim.*, Series 3, vol. xix.-xx., No. 12.

SOLUTIONS OF SILICATES OF THE ALKALIES.*

By LOUIS KAHLENBERG and AZARIAH T. LINCOLN.

(Concluded from p. 33).

The lithium silicates investigated yielded the figures in Tables VI. and VII. The normal salt is decomposed to the extent of 95·5 per cent at $v=32$, while at $v=48$ the decomposition is practically complete, as in the case of the analogous sodium and potassium salts. The salt $Li_2Si_5O_{11}$ is hydrolytically dissociated 67·7 per cent, and this decomposition is practically complete at $v=128$. The behaviour of the lithium salts, then, is perfectly analogous to that of the potassium and sodium salts.

The determinations made with rubidium and cæsium silicates are given in Tables VIII. and IX. The quantities of these alkalies that were available were small, and hence but few determinations were made. A glance at the results shows that these silicates behave like those of the other alkalies. The solutions investigated were quite dilute, and in them, as the results show, the hydrolytic decomposition had gone on very far. The lowerings obtained with the rubidium salt are greater than they ought to be theoretically. This is probably due to the fact that the rubidium salt, from which the hydroxide of rubidium that was used was prepared, contained some sodium. As the quantity of rubidium salt available was small a special analysis to ascertain the amount of sodium present was not made.

The results of the determinations of the electrical conductivity of the solutions are contained in Tables X. and XI. The former table contains the conductivity of solutions of the free alkalies at 25° C. It was necessary to make these determinations, for the conductivity of solutions of the alkaline hydroxides at 25° C. could not be found in the literature, and only by comparing the conductivity of solutions of the alkaline silicates with that of solutions of the free alkalies, can an idea of the extent of the retarding influence that the colloidal silicic acid has on the movements of the ions, be gained.

Kohlrausch (*loc. cit.*) noticed that on diluting silicate solutions the conductivity changed for a time and finally became constant. The time of this variation and the degree of the latter depended of course on the conditions

Table VII.

$Li_2Si_5O_{11}$. Molecular weight = 329·52.

v.	Freezing-point.	Mol. wt.	Mol. wt. (LiOH).
32	0·172	113·2	16·4
48	0·139	93·3	13·5
64	0·112	86·9	12·6
96	0·077	84·3	12·2
128	0·062	78·5	11·4

¼ of 329·52 = 82·38.

Table VIII.

Rb_2SiO_3. Molecular Weight = 245·38.

v.	Freezing-point.	Mol. wt.	Mol. wt. (RbOH).
64	0·139	52·1	43·2
96	0·098	49·3	40·9

¼ of 245·38 = 61·34. ½ Mol. wt. RbOH = 50·83.

Table IX.

Cs_2SiO_3. Molecular Weight = 339·60.

v.	Freezing-point.	Mol. wt.	Mol. wt. (CsOH).
64	0·102	98·3	86·1
96	0·068	98·3	86·0

¼ of 339·60 = 84·9. ½ Mol. wt. CsOH = 74·38.

Table X.

v	NaOH. λ	KOH. λ	LiOH. λ
1	157·5	—	—
2	181·2	196·7	157·6
4	188·1	207·2	171·0
8	194·7	213·1	179·2
16	197·4	216·7	185·9
32	199·0	219·1	189·3
64	199·1	220·4	189·2
128	199·0	218·4	189·2
256	196·3	215·0	184·0
512	188·9	208·0	174·9
1024	181·8	201·4	170·0

The water used had a specific conductivity of $1·7 \times 10^{-6}$. This has not been deducted in the above table.

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* *Journal of Physical Chemistry*, vol. ii., No. 2, February, p. 77 (1898).

TABLE XI.

	Na_2SiO_3.	$NaHSiO_3$.	$Na_2Si_5O_{11}$.	K_2SiO_3.	$KHSiO_3$.	Li_2SiO_3.	$Li_2Si_5O_{11}$.
v	λ	λ	λ	λ	λ	λ	λ
8	105·3	72·4	—	—	87·3	—	—
16	112·0	78·8	—	130·9	110·3	—	—
32	117·8	84·9	73·0	176·4	117·6	125·0	55·4
64	115·0	90·1	79·9	182·6	126·2	126·0	61·6
128	119·5	103·7	87·3	185·5	133·4	129·2	67·5
256	95·7	114·2	93·1	187·1	141·7	130·2	72·6
512	91·8	133·1	101·1	191·8	155·9	138·5	78·9
1024	104·8	148·5	113·3	182·5	175·6	145·2	90·6

The conductivity of the water, which was 1×10^{-6}, has been deducted in each case.

of experiment. Kohlrausch investigated this time factor as well as the variation of the conductivity of sodium silicate solutions with the temperature. He found that in some cases equilibrium was established in the solution in a few minutes, in others it took five hours or more. The time effects studied by Kohlrausch were also observed by us, and on the whole we are able to confirm his experiments as far as we went. It was not the purpose of this investigation, however, to study this time effect further, and for this reason the conductivity of the solutions was determined only after equilibrium had become established in them. The strongest silicate solution was prepared as already described, then the various dilutions (v = 16 to 1024) were prepared in thoroughly cleaned and steamed flasks, which were kept tightly corked. The dilutions were made by means of carefully calibrated pipettes. At the end of five to six hours (when equilibrium had practically become established) the contents of the various flasks were quickly transferred to the resistance cell and the conductivity determined.

In Tables X. and XI. v denotes the volume in litres in which one grm.-equivalent of the compound indicated by the formula is contained, and λ denotes the equivalent conductivity expressed as usual in mercury units.

It will be observed that in Table X. the values for λ increase as v increases until they reach a maximum, after which they decrease. This behaviour of the alkaline hydroxide is well known and is to be ascribed to impurities in the water. Table XI. shows that in case of the normal silicates of sodium and potassium the values for λ also pass through a maximum. In case of the acid silicates of sodium and potassium and those of lithium the values for λ do not pass through a maximum. It will be noted that the conductivity of the normal salts is uniformly greater than that of the acid salts of the same metal. The values of λ for v = 256 to 1024 in the case of Na_2SiO_3 are less than those for the acid silicates at the same concentrations; this, however, is undoubtedly due to experimental error. A re-determination of λ for these concentrations was contemplated, but was not carried out, as it is especially difficult to get a mixture of the silicic acid solution and caustic soda in the proportions required by the formula Na_2SiO_3, owing to the fact that the mixture gelatinises just before the entire quantity of alkali has been added.

By comparing the values for λ in Table X. with those of the salt of the corresponding metal in Table XI. the effect of the presence of the silicic acid on the conductivity may be seen. It will be observed that even in the most dilute solutions of the normal salts the values for λ still fall considerably short of equalling those of the hydroxides. The values of λ in Table X. pass through their maximum at about v = 32 to 64; at this concentration then the hydroxides are practically completely dissociated. It will be recalled that from the cryoscopic determinations on the normal silicate solutions it was inferred that in the latter hydrolytic decomposition is practically complete at v = 48. Although the errors of measurement in the freezing-point determinations are greater than in the measurement of the electrical conductivity, yet it would appear safe to say that the increase in the value of λ for the silicate solutions beyond v = 64, is mainly due to a decrease of the retarding influence of the silicic acid on the movements of the ions.

The conductivity of solutions of cæsium and rubidium silicates was also determined. Unfortunately the water used in making the dilutions had become contaminated, a fact which was later discovered, and hence the figures obtained are not given here. It may be stated, however, that the figures obtained showed beyond any reasonable doubt that the silicates of these alkalies behave in a manner entirely analogous to that of the silicates of the other alkalies.

Summary of Results and General Remarks.

The results of the foregoing investigation may be briefly summarised as follows:—

1. The conclusion of F. Kohlrausch that in solutions of sodium silicates these salts are hydrolytically decomposed into sodium hydroxide and colloidal silicic acid, has been confirmed by investigating the freezing-points of such solutions.

2. The freezing-points and the electrical conductivity of solutions of the silicates of potassium, lithium, rubidium, and cæsium show that these salts are also decomposed by water into the colloidal silicic acid and the hydroxide of the alkali metal. The silicates of the alkalies all show an analogous behaviour when dissolved in water.

3. The same solution results whether a silicate is dissolved in water or whether solutions of caustic alkali and colloidal silicic acid in proper proportions are mixed.

4. Since colloidal silicic acid has but little effect on the freezing-point the degree of hydrolytic decomposition of the silicates can be calculated from the lowering of the freezing-point of their solutions.

5. Silicates of the general formulæ M_2SiO_3 and $MHSiO_3$ are practically completely hydrolytically dissociated when one grm.-molecule is contained in 48 litres. Silicates of the general formula $M_2Si_5O_{11}$ are practically completely decomposed by water when one grm.-molecule is present in 128 litres.

6. A comparison of the electrical conductivity of silicate solutions with that of the solutions of the alkaline hydroxides, shows that the values of the former approach the latter as the solutions become more dilute, the retarding influence that the silicic acid has on the mobility of the ions gradually becoming less.

The conclusions here arrived at are of general interest inasmuch as silicates occur in greater or less quantities in almost all natural waters. If the silicates of the alkalies are so easily decomposed by water, how much more readily would silicates of the alkaline earths and the heavier metals be hydrolytically decomposed, especially since solutions of these salts are always exceedingly dilute because the compounds are so difficultly soluble.

Of the waters of 859 springs in various parts of the United States (see *Bull. U. S. Geol. Survey*, 32, 35, 1886), the one that contains the most silica is that of the Deep Rock Mineral Spring at Oswego, N.Y. According to an analysis made in 1871 by S. H. Douglas it contains the molecular weight of SiO_2 in grms. in 48·84 litres.* Next to this is Opal Spring in Yellowstone National Park in the Gibson Geyser Basin, for according to an analysis made by Henry Leffmann in 1882, its water contains one grm.-molecule SiO_2 in 65·15 litres. The analyses of the other 857 springs show that the waters of but three of them contain over one grm.-molecule SiO_2 in 140 litres and only fourteen others contain more than a grm.-molecule in 350 litres. The waters of the remaining 840 springs contain much smaller amounts of silica, usually less than one grm.-molecule in 3500 litres.

Justus Roth's (*Allgemeine u. Chemische Geologie*, vol. i.) compilation of the analyses of river waters from different parts of the globe (chiefly European, however) shows that the largest amount of silica was found in the water of the Rhine. A sample taken near Strassburg contained one grm.-molecule SiO_2 in 1250 litres. According to the same authority the Atlantic Ocean contains one grm.-molecule SiO_2 in 531 litres. Of the many analyses of the waters of springs of various kinds located in different parts of the globe that have been collected by Roth, none show a greater content of silica than one grm.-molecule in 80 litres, and of course most of them very much less.

In the face of these facts and the results of the above investigations it appears safe to say that in natural waters silicic acid always occurs in the colloidal state; only in very rare instances are the solutions of the silicates so concentrated that they are not practically completely hydrolytically decomposed. This conclusion will no doubt be of value to the mineralogist and geologist in explaining the formation of various siliceous deposits and the alterations produced in rocks by the action of water. It might also prove to be of value to the plant physiologist in explaining how plants take up various constituents from the soil.

TERRESTRIAL CORONIUM.

Professor Nasini, of Padua, who has been working in conjunction with Signori Anderlini and Salvadori, communicates the following note to the French Academy:—

We have for a considerable time been occupied with an extensive study of the gases emanating from the earth in various parts of Italy with the object of detecting the presence of argon and helium, and possibly of other elements they may contain.

The first part of this work has already been published ("Gas delle terme di Abano," *Gazzetta Chemica Italiana*). We are now completing the study of the gases of the Solfatara di Pozzuoli, Grotta del Cane, Grotta ammoniacale, and of Vesuvius. In the spectrum of those of Solfatara di Pozzuoli, which contain argon, we have found a sufficiently bright line with the wave-length 531·5, corresponding to that of corona 1474 K, attributed to coronium, an element not yet discovered, and which should be lighter than hydrogen. This line has never before been observed in earthly products. Besides, we have noted the following lines:—653·5, 595·5, 536·2.

In the spectrum of the gases gathered from the fumarole of Vesuvius, we have observed the lines 769·5, 631·8, 572·5, 536·5, 441·5, and again 595·5. These lines do not all belong to the spectrum of argon or helium; they show a coincidence or proximity only with some unimportant lines of various elements, such as iron, potassium, and titanium. Considering the conditions of our experiments the presence of these elements in the gases we have studied is not probable. The line 572·5 is near to one of nitrogen, but, being the only visible line of the spectrum of this gas, it cannot be attributed to it. Besides coronium we have thus probably other new elements in these gases.

We are diligently pursuing their investigation.

This is an announcement of the highest interest from a scientific point of view, as at once confirming the results of spectroscopic examination of the sun and adding another proof of the substantial identity of materials in the sun and the earth. Hitherto nothing has been known of the substance which produces the coronal line 1474 K. It has not been observed anywhere in nature except in the corona, its supposed identity with the auroral line having long ago been disproved, although it may possibly be asserted here and there in a text-book not written up to date. Coronium would seem, however, to be a substance with a vapour density far smaller than that of hydrogen, which is by far the lightest body with which we are familiar. Some have suggested that it is only one of the elements known to us, modified in some unknown way by conditions differing enormously from those that obtain on this planet. But against this hypothesis has to be set not only its occurrence at a distance from the sun's body estimated at 300,000 miles, where it is difficult to believe that the vapours of the suggested elements can predominate, but also the fact that in the midst of solar disturbances in prominences or near sun spots, when the lines of hydrogen and other known elements are contorted, this coronal line remains sharp, fine, and straight. From these and other considerations it has been held that the green coronal line is due to a permanent component of the solar atmosphere totally distinct from any element known to terrestrial chemistry. That unknown substance appears now to have been found just where, if anywhere on earth, it might be expected—*i.e.*, in the gases from volcanoes or the springs and minerals subject to volcanic action. It will be observed that even with this addition to the list of known elements the lines in the spectra of the volcanic gases cannot be completely accounted for. It is therefore probable that coronium will be found to be associated with other gases as yet unnoticed.—*The Times*, July 20, 1898.

SOME PRINCIPLES AND METHODS OF ANALYSIS APPLIED TO SILICATE ROCKS.*

By W. F. HILLEBRAND.

Part I.—*Introduction.*

The composition of the ultimate ingredients of the earth's crust—the different mineral species which are there found and of many of which its rocks are made up—was the favourite theme of the great workers in chemistry of the earlier half of this century, and for the painstaking care and accuracy of Berzelius, Wöhler, and others, the mineralogists and geologists of to-day have need to be thankful. Considering the limited facilities at their disposal in the way of laboratory equipment and quality of reagents, the general excellence of their work is little short of marvellous. As an outgrowth of and closely associated with the analysis of minerals, came that of the more or less complex mixtures of them,—the rocks,—to aid whose study by the petrographer and geologist a host of chemists have for many decades annually turned out hundreds of analyses of all grades of quality and completeness. With the growth and extraordinary development of the so-called organic chemistry, inorganic chemistry gradually fell into a sort of disfavour. In many, even of the best, European laboratories the course in mineral analysis, while maintained as a part of the curriculum of study, became but a subordinate prelude to the ever-expanding study of the carbon compounds,

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* It seems almost that the figures in the report must be a misprint.

* From the *Bulletin of the United States Geological Survey*, No. 148, p. 15, 1897.

whose rapid multiplication, offering an easy and convenient field for original research and possible profit, proved a more tempting opening to young chemists than the often-worked-over and apparently exhausted inorganic pasture. For one student devoting his time to higher research on inorganic lines were perhaps fifty engaged in erecting the present enormous structure of carbon chemistry. The instruction afforded the student in mineral analysis was confined to the ordinary separations of the commoner ingredients occurring in appreciable quantities, with little regard to supposed traces, and with still less attempt to find out if the tabulated list really comprised all that the mineral or rock contained.

With the introduction of improved methods of examination by the petrographer, especially as applied to thin rock sections and the use of heavy solutions, whereby, on the one hand, the qualitative mineral composition of a rock could be preliminarily ascertained with considerable certainty, and on the other, chemical examination of the more or less perfectly separated ingredients was rendered possible, a great help and incentive was afforded to the few chemists engaged in rock analysis. The microscope often obviated in part the necessity for tedious and time-wasting qualitative tests, and the heavy solutions, by permitting the concentration and separation of certain components, facilitated the detection of elements whose existence had long been overlooked.

Meanwhile in the progress of chemistry new methods and reagents for qualitative detection and quantitative separation and estimation were gradually being discovered and devised. The supposed adequacy of some well-established methods was shown to be unwarranted; some had to be discarded altogether; others were still utilisable after modification. In the light thus shed it became possible to explain many hitherto incomprehensible variations in the composition of some rock species or types, as shown in earlier analyses, and in not a few cases it appeared that the failure to report the presence of one or more elements had obscured relations and differences which more thorough examination showed to exist (see pp. 44-45). Consequently there arose a feeling of distrust of much of the older work in the minds of those chemists and petrographers best qualified to judge of its probable qualities. This, and the incompleteness of nearly all the earlier work (and much of that of to-day unfortunately), as shown by the largely increased list of those elements now known to enter into the normal composition of rocks, is rendering the old material less and less available to meet the increasing demands of the petrographer.

And yet these demands on his part are, with few exceptions, by no means so exacting as they should be. Often the analysis is intrusted to the hands of a student without other experience than that gained by the analysis of two or three artificial salts and as many comparatively simple natural minerals, and with a laboratory instructor as adviser whose experience in rock analysis may be little superior to his own. In other words, one of the most difficult tasks in practical analysis is expected to be solved by a tyro, and his results are complacently accepted and published broadcast without question. Even to those thoroughly familiar with the subject, rock analysis is a complex and often trying problem. Although long practice may have enabled one to do certain parts of it almost mechanically, he is still from time to time confronted with perplexing questions which require trained judgment to properly meet and answer, and there is still room for important work in some of the supposedly simplest quantitative determinations. If the results are to be of any decided value for purposes of scientific interpretation and comparison, they should be the product of one competent to find his way through the intricacies of an analysis in which from fifteen to twenty-five different components are to be separated and estimated with close approach to accuracy, and this a beginner cannot hope to do in the majority of cases. The conscientious chemist should have a live interest in this matter. He should work with a twofold purpose in view—that of lightening the labours of those who come after him, by enabling them to use his work with less supplementary examination, and of thereby enhancing his own reputation by meriting encomiums on work that has stood the test of time.

The petrographer, again, should seek to have his analyses made as complete as posssible, and not, as is so often the case, be content with determinations of silica, alumina, the oxides of iron, lime, magnesia, the alkalies, and water. The latter, it is true, are entirely justifiable at times, and may serve the immediate purpose for which they were intended; but their incompleteness may, on the other hand, not only conceal points fruitful of suggestion to the attentive mind, but—what is of still greater importance—they may be actually misleading. Enough instances of totally inaccurate conclusions to be drawn from them have fallen under my own observation to fully justify this plea in favour of greater completeness in rock and mineral analyses made for purely scientific purposes.

This is shown by the difference between the following analyses:—

	Earlier analysis.	Later analysis. (*a*)
SiO_2	54·42	53·70
TiO_2	—	1·92
Al_2O_3	13·37	11·16
Cr_2O_3	—	0·04
Fe_2O_3	(*b*) 0·61	3·10
FeO	(*b*) 3·52	1·21
MnO	—	0·04
CaO	4·38	3·46
SrO	—	0·19
BaO	—	0·62
MgO	6·37	6·44
K_2O	10·73	11·16
Na_2O	1·60	1·67
Li_2O	Trace	Trace
H_2O below 110° C.	—	0·80
H_2O above 110° C.	(*c*) 2·76	2·61
CO_2	1·82	—
P_2O_5	—	1·75
SO_3	—	0·06
F	—	0·44
Cl	—	0·03
	99·58	100·40
Less O for F		0·19
		100·21

(*a*) A still more recent analysis of another of the series of rocks of which this is an example has shown that this "later analysis" is itself probably incomplete and incorrect in part—incomplete because of the probable presence of 0·2 per cent or more of ZrO_2, incorrect because of the error in Al_2O_3 resulting from having counted the ZrO_2 as Al_2O_3, and from the fact that titanium is not fully precipitable in presence of zirconium by Gooch's method (the one employed). This latter error involves both the TiO_2 and the Al_2O_3.

(*b*) From the fact that repeated determinations of the iron oxides in this and related rocks from the same region show always a great preponderance of ferric oxide, it is not improbable that the figures given for the two oxides in the first analysis were accidentally transposed.

(*c*) In the published analysis it does not appear whether this is total water or—as seems probable—only that remaining above 100° C.

The specimens were taken and analysed at widely separated times and by different persons, it is true, but they were unquestionably from the same rock mass, in which, however much the relative proportions of the different mineral constituents might vary within certain limits, there can be no reason to doubt the general distribution of all the elements shown by the second analysis.

Another instance of similar kind is given below. Here, again, certain differences are explainable by natural variations in the proportions of the constituent minerals; but it can hardly be doubted that TiO_2, BaO, SrO, P_2O_5, and SO_3 were present in both specimens in approximately the same amounts. In the earlier analysis in this case determinations of some supposed unimportant constituents were purposely omitted or only made qualitatively, with results that cannot be otherwise than fatal to a full comprehension of the mineralogical nature of the rock:—

	Earlier analysis.	Later analysis.
SiO_2	44·31	44·65
TiO_2	Not est.	0·95
Al_2O_3	17·20	13·87
Fe_2O_3	4·64	6·06
FeO	3·73	2·94
MnO	0·10	0·17
CaO	10·40	9·57
SrO	—	(*a*) 0·37
BaO	—	0·76
MgO	6·57	5·15
K_2O	3·64	4·49
Na_2O	4·45	5·67
Li_2O	—	Trace
H_2O below 110° C.	0·77	0·95
H_2O above 110° C.	—	2·10
H_2O by ignition ..	3·30	—
CO_2	—	0·11
P_2O_5	—	1·50
Cl	—	Trace
SO_3	—	0·61
	99·11	99·92

(*a*) Not entirely free from CaO.

In order to more strongly emphasise the importance of completeness in analysis, one fact brought out by the hundreds of rock analyses made in this laboratory may be cited. It has been demonstrated most conclusively that barium and strontium are almost never-failing constituents of the igneous rocks and many of their derivatives of the United States. These amounts are usually below 0·1 per cent for each of the oxides of these metals, but higher amounts are by no means uncommon. Furthermore, the weight of barium is almost without exception in excess of that of strontium. But a still more important point is that the igneous rocks of the Rocky Mountain region, so far as examined, show far higher average percentages of both metals than the rocks from the eastern and the more western portions of the United States. The following examples serve to illustrate certain types of Rocky Mountain igneous rocks:—Of seven rocks forming a Colorado series, six held from 0·13 to 0·18 per cent of BaO, while in the seventh the percentage was 0·43. The SrO ranged from 0·07 to 0·13 per cent for six, and was 0·28 for that one highest in BaO. Of thirteen geologically related rocks from Montana, embracing basic as well as acid and intermediate types, the range of BaO was from 0·19 to 0·37 per cent, with an average of 0·30 per cent. Three others of the same series contained 0·10 per cent or less, while the seventeenth carried 0·76 per cent BaO. The SrO ranged from 0·37 per cent in the last instance to an average of 0·06 for the other sixteen. Certain peculiar rocks from Wyoming carry from 0·62 to 1·25 per cent BaO, and from 0·02 to 0·33 per cent SrO. Surely this concentration of certain chemical elements in certain geographic zones has a significance which future geologists will be able to interpret if those of to-day are not.

While strongly upholding the necessity for more thorough work, necessarily somewhat at the expense of quantity, it is far from the writer's intention to demand that an amount of time altogether disproportionate to the immediate objects to be sought should be expended on every analysis. But it is maintained that in general the constituents which are likely to be present in sufficient amount to admit of determination in the weight of sample usually taken for analysis—say 1 grm. for SiO_2, Al_2O_3, &c., to 2 grms. for certain other constituents—should be sought for, qualitatively at least, in the ordinary course of quantitative work, and their presence or absence noted among the results. If present in little more than traces, that knowledge alone may suffice, for it is often more important to know whether or not an element is present than to be able to say that it is there in amount of exactly 0·02 or 0·06 per cent. In the tabulation of analyses a special note should be made in case of intentional or accidental neglect to look for substances which it is known are likely to be present. Failure to do this may subject the analyst to unfavourable criticism, when at some future time his work is reviewed and the omissions are discovered by new analyses.

Finally, whenever possible, a thorough microscopical examination of the rock in thin section should precede the chemical analysis. This may be of the greatest aid to the chemist in indicating the presence of unusual constituents, or of more than customary amounts of certain constituents, whereby, possibly, necessary modifications in the analytical procedure may be employed without waste of time or labour.

(To be continued).

NOTICES OF BOOKS.

A Course of Practical Chemistry, or Qualitative Chemical Analysis. By the late W. G. Valentin, F.C.S. Edited and Revised by W. R. Hodgkinson, Ph.D., F.C.S., &c., Professor of Chemistry and Physics in the Royal Military Academy and Artillery College, Woolwich. Ninth Edition. Pp. 403. London: J. and A. Churchill. 1898.

We are glad to welcome yet another edition of this excellent and well-known work. It is many years since the first edition appeared, and, as time has gone on, so has this book gone on "with the times," dropping parts which were of little value, and, so to say, filtering itself, while at the same time keeping up with all that is new in this particular branch of chemical science.

The plan of the book is the same as in previous editions, and is familiar to all chemists; the principal alteration in this edition being the addition of an extra chapter, or rather appendix, in which simple quantitative, including volumetric, operations are dealt with.

More experimental matter has been added, and this is a point to be remembered and dwelt upon, as there is no doubt that a young student will retain far more knowledge if he has to do practical work with his own hands than by merely reading for so many hours a day, getting ready for the inevitable "exam."

Dr. Hodgkinson is not wedded to the "cram and exam." idea, but, on the contrary, takes a keen personal interest in each and all of his pupils, and should be able to "place" them in as satisfactory an order as any examiner.

We cordially recommend this book to beginners in chemistry, as well as to those who have reached a more advanced stage, while at the same it will always be useful as a book of reference.

Elementary Chemistry, Practical and Theoretical. First Year's Course. By T. A. Cheetham, F.C.S. London: Blackie and Sons, Lim. 1898. Pp. 128.

This book, like so many others, is purely for the beginner in chemistry. It commences with exercises in manipulation, the first 65 pages being devoted entirely to laboratory—that is, experimental—work, after which we come to the more theoretical side of the subject.

In the two chapters on air, its synthesis, &c., we are rather surprised to find no mention of any gas beyond oxygen and nitrogen; surely it is long enough ago since argon was discovered for inclusion in a new text-book, even if the more recently announced elements are rather shadowy. This is, however, not a matter of great importance. Taking it altogether the book is conveniently planned, and is written in a clear and intelligible manner, and should fulfil the purpose for which it was written.

The Theory and Practice of Electrolytic Methods of Analysis. By Dr. Bernhard Neumann. Translated by J. B. C. Kershaw, F.I.C. London and New York: Whittaker and Co. 1898. Pp. 254.

In the translator's preface we read that only a small number of corrections and alterations from the original have been found necessary, and these were made with the author's consent; the portion of the original work dealing with primary and secondry batteries, the dynamo, and the thermopile, has been omitted, and the electro-chemical equivalents have have been re-calculated upon the most trustworthy figures for the atomic weights of the elements.

The book is divided into three parts. Part I. is on the theory of electrolysis, and deals with Faraday's law, the constitution and conductivity of the electrolyte, the chemical and molecular changes during electrolysis, &c.

Part II., which is subdivided into sub-sections A and B, is on the measurement and regulation of the current. In Section A we find illustrated descriptions of all the well-known instruments used for current measurement, with instructions how to use them; Section B, which is of considerably more importance, is on regulating the current.

We then come to Part III., on the Electrolytic Procedure, divided into four sections:—A. Introductory; B. The deposition of metals from solutions of pure salts; C. Separation of the metals; and D. Practical examples. These four sections really comprise the pith of the book. The metals are dealt with *seriatim*, and all details and data for securing the best results are adequately given. Beginners should be reminded that a certain amount of discrimination is required as to when the electrolytic method may be employed with advantage over the chemical gravimetric method. In many cases the chemical method is preferable, especially if the greatest care has not been taken on the preparation of the electrodes. The current strength (E.M.F.) is another point which requires minute attention, as a very little increase beyond the proper strength will often entirely alter the character of the results.

On page 246 a useful table will be found, giving the theoretical percentage of the metals present in a certain number of metallic salts. The book closes with two indices—one for names, and the other for subject-matter.

CORRESPONDENCE.

THE NEW GASES.

To the Editor of the Chemical News.

Sir,—I observe that Professor Ramsay and his friends, at the fag-end of a letter to *Nature*, reply in an airy manner to the observations made by "Puzzled" in the Chemical News. They account for the attribution to metargon in Paris of a line ascribed to neon in London, by saying that there is a misprint in the *Comptes Rendus*. I have taken the trouble to look up the reference and I find that no possible correction of a misprint of names will meet the case. The line 5849·6 is given as characteristic of metargon in the midst of a description applying solely to that gas. To put neon for metargon in the only possible place, would transfer the whole paragraph to neon, and so make confusion worse confounded. On the other hand, if the misprint is supposed to occur in the figures designating the line in the spectrum, it is rather odd that Professor Ramsay does not mention the correct wavelength.

It would, perhaps, have been better had Professor Ramsay taken the letter of "Puzzled" with sufficient seriousness to reply deliberately in the journal where it appeared. This off-hand reference to a misprint for which there is no room, coming at the end of a rather inconclusive disquisition upon the unfortunate resemblance of the metargon spectrum to that of carbon, does not tend to strengthen public confidence in his general accuracy.—I am, &c.,

Suum Cuique.

THE YEARLY INDEX TO "THE JOURNAL OF THE CHEMICAL SOCIETY."

To the Editor of the Chemical News.

Sir,—I think that many others besides myself must suffer great inconvenience owing to the delay in the publication of the yearly index to the *Journal of the Chemical Society*. Although nearly seven months have elapsed since the completion of the last volume, the index is still not ready for publication. Not only does this prevent the binding of the volume, but renders the journal for 1897 practically valueless for reference. As I have addressed numerous unavailing remonstrances to the Secretary of the Chemical Society, I trust you will be kind enough to publish this note in the hope that some more general expression of opinion may be elicited.—I am, &c.,

A Fellow of the Chemical Society.

July 16th, 1898.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xix.-xx., No. 5.

Action of Alkaline Sulphites on the Chromic Salts. —A. Recoura.—If we add to a solution of a chromic salt a large excess of sulphite of sodium, we obtain a liquid in which the chromium has lost the greater part of its usual reactions. In such a solution, soda, carbonate of soda, ammonia, and sulphide of ammonium do not produce the precipitate of chromic hydrate which would come down in an ordinary solution of the salts of chromium. The author concludes that the cause of this anomaly is the immediate formation of a basic sulphate of chromium (these experiments were made with the sulphate) which unites with a certain number of molecules of sulphite of sodium, a number which cannot be exactly determined as the substance will not crystallise.

On Chloral-ammonia.—Marcel Delépine.—As chloral-ammonia cannot be volatilised without decomposition, the author had recourse to cryoscopy to decide what its true molecular weight is: he used successively benzene, acetic acid, and bromide of ethylene; but unfortunately the variations in passing from one solution to another are such that no very good results were recorded. However, two figures were obtained: M = 329 for a concentration of 3 per cent with benzene, and M = 335 with bromide of ethylene. To reconcile these results with Schiff's formula, both the benzene and the bromide of ethylene must be considered as allowing aggregates of molecules to be substituted, while they do not exist in acetic acid.

Thermo-chemistry: Hydramides and Isomerous Bases.—Marcel Delépine.—Recently distilled anisic aldehyd, $C_8H_8O_2$, boiling at 248—249°, gave as heat of combustion per grm., 7096·0, 7117·2, and 7110·1, average 7107·8 cals. That is, one molecule = 136 grms. The heat of combustion is:—

At constant volume	966·7 cals.
,, ,, pressure	967·3 ,,
Heat of formation—$C_8+H_8+O_2=C_8H_8O_2$ (liquid)	+63·1 ,,

The following heats of formation have also been found:—Anishydramide $(C_8H_8O)_3$, N_2(cryst.) = 48·4 cals.; anisine, $C_{24}H_{24}N_2O_3$ (solid), = +64·6 cals.; furfuramide $(C_5H_4O)_3N_2$ (cryst.), = +0·35 cals.; furfurine, $C_3H_{12}N_2O_3$ = 17·9. There is always a disengagement of 2 × 11 cals. for the formation of hydrobenzamide, and 13·9 cals. for its transformation into amarine.

Action of Bromine on Tetrabromide of Acetylene in the presence of Bromide of Aluminium. Preparation of Hexabromethane (C_2Br_6).—A. Mouneyrat.—The preparation of hexabromethane by the action of bromine and bromide of aluminium on tetrabromethane is described; it is rather a long process, but gives good results. The molecular weight of hexabromethane was determined by cryoscopy, using benzene—it was found to be 480; the calculated figure for C_2Br_6 is 504.

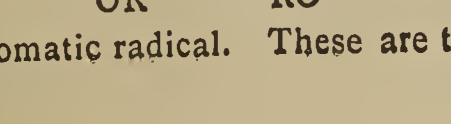
The Action of Chlorine on Chloroform in the presence of Chloride of Aluminium, and of Bromine on Bromoform in the presence of Bromide of Aluminium.—A. Mouneyrat.—The chloridising action of chloride of aluminium, and the bromidising action of bromide of aluminium in the ethane and in the higher series, shows that these two bodies have the property of creating ethylenic chains. In the methane series such a chain cannot be formed, with the result, from the chloridising and bromidising point of view, that the action is *nil*.

Action of Bromine on Pentachlorethane in the presence of Chloride of Aluminium. Preparation of Dibromotetrachlorethane, $C_2Br_2Cl_4$.—A. Mouneyrat.—This body, prepared from pentachlorethane, is obtained in perfectly defined orthorhombic prisms, smelling slightly of camphor; if left in a dry place they lose their transparency on account of their strong tendency to sublime. Heated in a capillary tube they begin to lose bromine at about 220—225°.

Action of Chloride of Aluminium on Pentachlorethane. Preparation of Bi-chloride of Carbon, $CCl_2=CCl_2$.—A. Mouneyrat.—Bichloride of carbon is obtained simply by heating chloride of aluminium with pentachlorethane; the reaction takes place at 70°, but if the temperature is raised to 100° it goes much more quickly; the return is absolutely theoretical.

Action of Bromide of Aluminium on Bromide of Ethylene, CH_2Br-CH_2Br.—A. Mouneyrat.—The author concludes from his experiments that bromide of aluminium also possesses the property of creating *ethylenic chains*, and can thus be a bromidising agent.

The Aromatic Diurethanes of Piperazine.—P. Cazeneuve and M. Moreau.—The authors thought that piperazine, which is a diazine possessing two NH in the nucleus, would act like two molecules of piperidine coupled. As a matter of fact they obtained with the phenolic carbonates bodies of the form—



$$CO{<}^{N}_{OR} \; N{<}^{C_2H_4}_{C_2H_4}{>}N \; {}^{N}_{RO}{>}CO\ ;$$

R being an aromatic radical. These are true piperazinic diurethanes.

Aromatic Urethanes of Conicine.—P. Cazeneuve and H. Moreau.—The authors have prepared three urethanes of conicine, viz., the phenylic, the gaiacolic, and the α and β naphtholic. The gaiacolic and naphtholic derivatives have undoubtedly a rotatory power, but not enough was prepared to enable this to be measured.

Action of Chloride of Titanium, $TiCl_4$, on some Organic Compounds.—M. Kling.—The action of $TiCl_4$ on pure aniline gives only fuchsine, leaving on calcination notable quantities of TiO_2. By its action on anisol, at first in the cold and then at 200° in a sealed tube, there was an abundant disengagement of CH_3Cl, and a crystalline residue of ortho-titanate of phenyl was left.

Differential Reaction of Creosote and Gaiacols.—H. Fonzes-Diacon.—A scale of colours varying from a yellow-orange to a yellowish-green can be obtained similar to that described by M. Adrian, by treating, say, 10 c.c. of solutions made by dissolving 10 drops of gaiacols and creosotes in a litre of distilled water, by 2 c.c. of a solution of 0·5 grm. per 1000 of sulphate of copper, and 1 c.c. of a solution of 4 per 1000 of cyanide of potassium.

Journal de Pharmacie et de Chimie,
Series 6, vol. vii., No. 9.

The Estimation of Succinic Acid in the presence of Tartaric and Lactic Acids.—MM. Bordas, Joulin, and de Raczkowski.—(See p. 18).

The Activity of the Pancreatines.—Eug. Choay.—In the course of some recent work the author had occasion to prepare an aqueous extract of the pancreas of a pig. It occurred to him to make comparative experiments with it and commercial pancreatine, and he found the proteolytic power of the extract far superior to that of the commercial article of a brand very well known in pharmacy. The same was observed with regard to the power of liquefying starch paste. Other experiments were made on its action on fibrine, starch, and fat, and the conclusions drawn are: 1, that it is of great importance to assay all pancreatines; 2, that the aqueous extract of the pancreas concentrated in vacuo at a low temperature is an excellent preparation; 3, that pancreatine prepared carefully according to the Codex has the same activity as the aqueous extract on proteic and amylaceous materials. They only differ from that prepared *in vacuo* in that their power of saponification is greater.

Note on Salicylate of Methyl.—M. Adrian.—In view of the different boiling points given by different writers the author undertook some fractional distillations on two samples, one essence of winter-green and the other salicylate of methyl, and found that pure salicylate of methyl distils over between 220° and 223°, and that its density at 15° is from 1·15 to 1·20. It is nearly insoluble in water, but dissolves easily in alcohol and in ether. It takes a violet colour on the addition of perchloride of iron in a dilute aqueous solution. This ether is a true acid, and combines with potash, forming a crystalline salt. If we place one volume of methyl-salicylic ether in a stoppered flask with five or six volumes of concentrated ammonia, the ether disappears after a time; on the liquor being evaporated and the residue distilled, we obtain a yellow mass which crystallises in needles by dissolving in boiling water. This substance is salicylamide, which by the action of acids regenerates the ammonia in the form of a salt, and forms salicylic acid. The density and boiling point of salicylate of methyl are important indications of its purity; it may contain non-etherised methylic alcohol if the product is not properly washed, or methylic or ethylic alcohol added by fraud. The presence of either of these foreign bodies will notably lower the density and the initial point of distillation; a simple washing with distilled water will, however, suffice to purify the salicylate. This body may also be adulterated with a fixed oil, but the density will again be lowered, and, after distilling at 220°, a residue will be left, which will give off characteristic vapours of acrolein on being heated to a higher temperature.

MISCELLANEOUS.

South African Industrial and Arts Exhibition.—An Exhibition of the products, manufactures, and mineral wealth of the various States and Colonies of South Africa, together with the varied manufactures and merchandise which are or might be imported from other countries, will be held at Grahamstown in December, 1898. The recent great extensions of the South African railways will doubtless help this Exhibition to be even a greater success than the one held in 1887-88. Attention is directed to the fact that this Exhibition may serve to form the nucleus of a collection of articles illustrative of South African products and industries, to be sent to the Paris Exhibition of 1900. The diamond and gold industries will be specially represented, and the Rhodesian Government will do their utmost to show the latent wealth and resources of this new country. Exhibits from abroad will be brought from any port in the Colony, in bond, carriage free, and will not be subject to duty unless sold. It is expected that the steam-ship companies will carry exhibits from abroad at reduced rates. Diplomas and medals will be awarded to successful exhibitors in every department. The Exhibition will be opened on Thursday, December 15th, 1898, and will be closed on Saturday, January 21st, 1899. It will be divided into five principal groups:—A. Raw Materials; B. Manufactures; C. Mining and Machinery; D. Natural History and Science; E. Fine Arts. These again will be subdivided into a number of sections and groups. Schedules of application for space may be had from the Secretary, Mr. G. B. Wedderburn. These must be filled up and returned by October 31st. Messrs. William Savage and Sons, Blomfield House, London Wall, E.C., have been appointed the Agents in London, and will supply all further information.

THE CHEMICAL NEWS.

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ON POLONIUM: A NEW RADIO-ACTIVE SUBSTANCE CONTAINED IN PITCHBLENDE.

By P. CURIE and Mdme. S. CURIE.

Certain minerals containing uranium and thorium (pitchblende, chalcolite, uranite) are very active from the point of view of the emission of the new rays described by M. Becquerel. In a previous work one of us showed that their activity is even greater than that of uranium and thorium, and expressed the opinion that this effect was due to the presence of another very active substance in these minerals, though in very small quantities (Mdme. S. Curie, *Comptes Rendus*, cxxvi., p. 1101).

The continued study of the compounds of uranium and of thorium have shown, as a matter of fact, that the property of emitting rays which make the air a conductor, and which also act on photographic plates, is a specific property of uranium and thorium, both of these being present in all these compounds, but this characteristic is weaker as the proportion of the active metal present in the mineral is smaller. The physical condition of the metal seems to be of an altogether secondary importance. Various experiments have shown that the conditions of mixture of these substances does not seem to have any effect except in varying the proportion of the active bodies, and the absorption produced by the inert matter. Certain causes (such as the presence of impurities), which act in such a powerful manner on phosphorescence and fluorescence, are in this case entirely inert. From this fact it appears very probable that if certain minerals are more active than are uranium and thorium, it is due to the fact that they contain a substance more active than either of these two metals.

We have endeavoured to isolate this substance from pitchblende, and experiment has confirmed our previous ideas.

Our chemical researches have been constantly guided by the confirmation of the radiant activity of the products separated by each operation. Every product was in turn placed on one of the plates of the condenser, and the conductivity acquired by the interposed air was measured by means of an electrometer and the apparatus already described in a previous paper. We have thus not only an indication, but an actual scale which shows the richness of the body in degrees of the active substance.

The pitchblende which we analysed was about twice and a half more active than the uranium used in our plate apparatus. We have attacked it with acids, and treated the solution formed with sulphuretted hydrogen. The uranium and the thorium remained in solution. We also noted the following facts:—

The precipitated sulphides contain a very active substance besides lead, bismuth, copper, arsenic, and antimony.

This substance was perfectly insoluble in sulphide of ammonium, which separated it from the arsenic and antimony.

The sulphides insoluble in sulphide of ammonium were dissolved in nitric acid; the active substance can be partially separated from the lead by means of sulphuric acid. By exhausting the sulphate of lead by means of dilute sulphuric acid we can to a great extent dissolve the active material which has been carried down with the lead.

This substance, now in solution with bismuth and copper, is completely precipitated by ammonium, which separates it from the copper.

Finally, this active body remains, in company with bismuth.

We have not yet succeeded in finding any method of separating these two bodies by the wet way. We have, however, succeeded in making partial separations based on the following facts:—

In the solution of the sulphides in nitric acid, the easiest parts to dissolve are the least active. In the precipitation of the salts by water the precipitated portions are much the most active.

We have also observed that by heating pitchblende we obtained a very active body by sublimation. This observation has led us to a process of separation founded on the different volatility of the active sulphide and the sulphide of bismuth. The sulphides are heated in vacuo in a Bohemian glass tube to about 700°. The active substance is deposited in the form of a black film in that portion of the tube which is between 250°—300° temperature, while the sulphide of bismuth remains in the warmer part of the tube.

By carrying out these various operations we obtain products of greater and greater activity.

Finally, we obtained a body of which the activity is 400 times greater than that of uranium.

We have searched among all known elements for any with such activity. We have examined the compounds of nearly all the similar bodies; thanks to the kindness of many chemists we have had the use of samples of the most rare bodies. Uranium and thorium alone are practically active: tantalum is so perhaps to a very feeble extent.

We therefore believe that the substance we have isolated from pitchblende contains a hitherto unknown metal, very similar to bismuth in its analytical properties.

If the existence of this new metal is confirmed we propose for it the name *Polonium*, after the native country of one of us.

M. Demarçay has been kind enough to examine the spectrum of the body we have found, but he has not been able to distinguish any characteristic line except those due to impurities.

This fact does not favour the idea of the existence of a new metal. However, M. Demarçay reminds us that uranium, thorium, and tantalum give peculiar spectra, formed of innumerable fine and difficultly seen lines. (M. Demarçay, "Spectres Electriques," 1895).

May we be permitted to add, that if the existence of a new simple body is confirmed, this discovery will be entirely due to the new method of investigation given to us by the rays discovered by M. Becquerel.—*Comptes Rendus*, vol. cxxvii., No. 3, July 18, 1898.

ON THE MIXED HALOGEN SALTS OF LEAD.

By V. THOMAS.

If the history of the halogen salts of lead is now familiar to us the same cannot be said of the history of the mixed salts, combinations of the chloride and iodide, the chloride and bromide, the bromide and iodide, in spite of the number of chemists who have taken up the study.

It is the study of this question that I have recently been engaged on.

Chloroiodides of Lead.—The chloroiodides of lead may be formed:—

1. By dissolving an iodide in hydrochloric acid.
2. By the mixture of an alkaline iodide with chloride of lead.
3. By the solution of iodide of lead in an alkaline chloride.

4. By boiling a solution of chloride of lead with iodide of lead.

These methods have been successively applied with more or lese success by Labouré, Dietzel, Poggiale, Engelhardt, Miss Field, and by Herty.

Labouré (*Journ. de Pharm. et de Chim.*, Series 3, vol. iv., p. 328), by treating iodide of lead with boiling hydrochloric acid, obtained a red solution, which on cooling produced prismatic crystals. But the author did not submit these crystals to analysis; the experiment was afterwards repeated by Dietzel (*Dingl. Polyt. Journ.*, vol. cxc., p. 41). This chemist gave it the formula $PbICl$.

In the year 1845 Poggiale (*Comptes Rendus*, vol. xx., p. 1180), described several double haloids, and in particular a chloroiodide of lead, which he obtained by treating a solution of chloride of lead with iodide of sodium, or by dissolving iodide of lead in chloride of ammonium. Poggiale gave it the formula $PbI2,2PbCl_2$. It is to be regretted that the original memoir did not mention the relative proportions of the salts necessary to obtain this compound.

Engelhardt (*Journ. f. Prakt. Chim.*, vol. lxvii., p. 293; 1856), in a long paper on the action of metallic chlorides on iodide of lead, again took up the question. He first of all studied the action of iodide of lead on the chloride. According to this writer, by boiling a certain quantity of iodide of lead in water, in the presence of an excess of chloride of lead, the iodide of lead is rapidly transformed into a yellow powder. The liquor, when left to cool, deposits white crystals in the form of needles; these crystals are nothing else but the chloride. As for the yellow powder, by boiling it up again with water, which partially dissolves it, we obtain a solution which on cooling gives very good crystals of a yellow colour, very much in the form of needles. The residue again treated with water leaves another residue, and also gives a solution which, under favourable circumstances, deposits small crystals analogous to those already mentioned, but of a much deeper colour.

If instead of treating a mixture of the iodide and the chloride by water, we mix the warm solution of these two salts we arrive at the same results as before, which are:—

1. The percentage of lead in the first compound is 68·93.

2. The proportion of lead present diminishes as the number of treatments by water increases. The crystals isolated the second time contain 59·35 per cent of lead. Engelhardt has slightly varied the conditions of this experiment. Instead of successively treating the different yellow residues with boiling water, in a second series of experiments he took up the residues with the corresponding filtrate from which the yellow crystals had already been allowed to separate by cooling. Under these conditions the estimations of the lead gave him figures intermediate between those already mentioned; that is to say, about 63·5 per cent.

To obtain similar results it is necessary to work not only in the presence of an excess of chloride of lead, but with solutions saturated with this salt.

When the iodide is in excess we obtain compounds in which the proportion of lead present is comprised between the limits $Pb = 56{\cdot}09$ and $Pb = 74{\cdot}5$.

The proportion of lead becomes less as the quantity of chloride used diminishes.

Engelhardt evidently considered these compounds as mixtures in varying proportions, since he proposed to include them all in the general formula:—PbI_xCl_y, a formula in which $x + y = 2$ with $x < 1$ and $y > 1$.

Instead of elucidating this question the work of the German chemist appears, on the contrary, more calculated to make the matter more indecisive than it was before he took the subject up.*

Miss Field (Chem. News, vol. lxvii., p. 157, 1893), has examined the mixed salts of lead over again, and shows that by heating together—

I.

PbI_2	1 grm.
AmCl	6 ,,
H_2O	50 ,,

a well crystallised chloroiodide was obtained. By boiling the mixture a yellowish powder is formed consisting principally of chloride and oxychloride with traces of iodide. By filtering the solution and leaving to stand till cold small green crystals are soon deposited. This filtrate contains chloride of lead and potassium, but no iodide. If these proportions are not exactly adhered to we get mixtures of chloride and iodide.

The author gives these green crystals, dried at 100°, the formula $PbICl + \frac{1}{2}H_2O$. By varying the proportions of the salts used Miss Field has succeeded in obtaining other compounds. For example, by boiling up—

II.

KI	1 grm.
$PbCl_2$	5 ,,
H_2O	250 ,,

and filtering the solution, we notice the formation of small green crystals which dissolve in water without decomposition, and which do not change colour when heated to 100°. According to the author it is difficult to obtain them in a state of purity, as they always entangle in them a small quantity of chloride and iodide. These crystals correspond to the two formulæ $3PbCl_2PbI_2$ and $5PbCl_2PbI_2$, no doubt according to the method of preparation used, but Miss Field does not show how we can prepare one or the other of them at will.

Finally, M. Herty (*Am. Chem. Journ.*, vol. xviii., p. 290), in quite a recent paper, has repeated Miss Field's experiments, and he concludes most decisively, although his conclusions do not appear according to his paper unassailable, that these compounds, until now regarded by him as chloroiodides of lead, are in reality nothing more than isomorphous mixtures of chloride and iodide.

I shall now examine successively the different methods proposed for the preparation of chloroiodides.

The Action of Hydrochloric Acid on Iodide of Lead.—The action of boiling concentrated hydrochloric acid on iodide of lead always gives rise to the formation of a corresponding chloroiodide having the formula $PbICl$, as shown by Dietzel. According to the length of the reaction and the relative proportions of the salt of lead and the acid present, so we obtain it in a state of purity, or mixed with iodide of lead. Analysis gives almost theoretical figures, although the figure for Cl is sometimes 0·5 per cent higher than the figure given by theory, viz.—theory, 9·63; found, 10·13.

This slight error with regard to the chlorine has made me suspect that the chloroiodide might in certain cases contain small quantities of chlorine as an impurity. This error is frequent if the estimation is made on large crystals, but if these are pulverised and the powder again dried on a porous plate, the preparation of chlorine found is almost exactly what is demanded by theory. Found, 9·59; calculated, 9·63.

The quantity of iodine found, no matter what the chlorine may be, is the theoretical amount: found, 34·42; calculated, 34·47. The same is the case with the lead; found, 56·01; calculated, 55·90.

These analytical results do not allow us to consider the presence of chloride of lead as an impurity. Further, we could not explain the presence of chloride of lead in the chloroiodide, even in a very minute quantity, as this body could only be formed by a previous decomposition of the iodide of lead, and must, therefore, *a fortiori*, be produced by the ebullition or the chloroiodide with the hydrochloric acid. Now the chloroiodide thus treated does not appear to undergo any modification, even after some considerable

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* I would here remark that the original paper did not contain the estimation of the halogen, either as a whole or separated (Cl + I or Cl.I), as far as it concerns the reciprocal action of the chloride and the iodide of lead.

time. It thus follows that the slight excess of chlorine sometimes shown by analysis is caused by a small quantity of hydrochloric acid being entangled in the crystals themselves.

To obtain the chloroiodide free from iodide of lead, it is necessary to work in the presence of a large excess of hydrochloric acid and also to keep the solution boiling for a considerable time; without this precaution, the iodide will be found to deposit the first on cooling, then only after some moments the chloroiodide appears, with a more or less abundant quantity of PbI_2.

The solution of chloride of lead in hydriodic acid does not enable us to prepare the chloroiodide, for it is a long known fact that hydriodic acid completely displaces hydrochloric acid from its salt of lead.

Reciprocal Actions of Alkaline Chlorides or Iodides with the Haloid Salts of Lead.—If we cause iodide of lead to react on a chloride, or an iodide on a chloride of lead, the question is entirely the same. In fact we find ourselves, by double decompositions, in the presence of a chloride and iodide of lead. The result I have achieved is extremely simple; I have never been able to prepare anything but a single compound, the chloroiodide, PbICl, either pure or more or less adulterated with chloride of lead. In particular, I repeated the experiments of Miss Field with the greatest care. Starting from the first system:—

I.

PbI_2	1 grm.
AmCl	6 ,,
H_2O	50 ,,

I always and very regularly obtained the body mentioned by this chemist. I would, however, point out that, while Miss Field attributed to the chloroiodide, dried at about 100°, half a molecule of water of crystallisation, I always found this salt anhydrous, as shown by the following analysis by drying in the cold on a porous plate. Found: Pb, 56·05; Cl, 9·22; I, 34·42. Calculated: Pb, 55·90; Cl, 9·63; I, 34·47.

It is this same anhydrous salt that I obtained by the second method:—

II.

KI	1 grm.
$PbCl_2$	5 ,,
H_2O	250 ,,

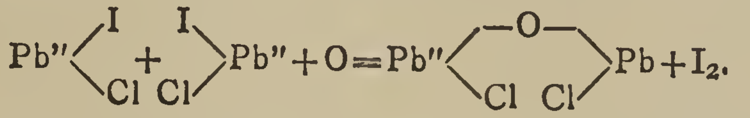
The chloride of lead (5 grms.) was dissolved in 240 c.c. of hot water, to which is added 10 c.c. of a one-tenth solution of iodide of potassium. The addition of iodide of potassium produces first of all a yellow precipitate which dissolves almost immediately, and at the same time deposits greenish crystals. This can further be fractionally crystallised by collecting the precipitate formed at 70°, 60°, 50°, 40°, &c., by successive coolings; it is necessary to go to a relatively low temperature (say 30°) to enable the microscope to reveal a mixture, and for analysis to show an excess of chlorine. The precipitates collected at first, and then at lower temperatures, such as 70°, 60°, 50°, and even 40°, corresponds exactly with the formula PbI.Cl.

Towards 10°, on the contrary, the precipitate is formed of chloride of lead, entirely free from any trace of iodide.

Must we then conclude that, according to the preceding method, it is only possible to produce a single chloroiodide of lead? No; but it seems now to be well proved that the chloroiodide of lead, PbICl, is a very stable compound and is formed with great facility. Other workers of greater experience may *perhaps* have been able to produce compounds differing from this one; but in any case is to be hoped that their chemical existence may be well proved. As for the chloroiodide, PbICl, its existence is proved by the product of oxidation which it is susecptible of forming when treated with peroxide of nitrogen.

I have had occasion to show (*These de Doctorat*, Gautier-Villars, 1897), that the different halogen compounds of lead behave in various manners with the hyponitride. In fact, while at the ordinary temperature the chloride and bromide were not attacked, the iodised compound was completely decomposed with the liberation of iodine and formation of oxide of lead, even at a low temperature. It should therefore be presumed that such a compound as PbICl treated by the hyponitride ought to give rise to the liberation of iodine and the formation of a corresponding oxychloride. It is this that experiment verifies; the displacement of the iodine commences in the cold, but it is necessary, to renew the active surfaces, to raise the temperature sufficiently to cause the sublimation of the iodine.

The decrease in weight observed is that required by the equation:—



Further, the estimation of the chlorine gives 14·14 against the theoretical figure 14·23.

The process which enables us easily to produce Matlockite gives the same facilities for distinguishing the mixtures of the iodides and chlorides, properly called chloroiodides. While the chloroiodides give rise to corresponding oxychlorides, the chlorides and the iodides behave differently. The chlorides are not attacked, and the iodides are transformed into oxides so completely that by treating the residue from the oxidation with warm water we can completely exhaust it, leaving a residue of pure oxide of lead.—*Bull. Soc. Chim.*, Series 3, vol. xix.-xx., No. 12.

AMMONIUM SELENIDE.

By VICTOR LENHER and EDGAR F. SMITH.

By bringing ammonia and hydrogen selenide together Bineau (*Ann. Chim. Phys.*, 2, 67, 227), claims to have prepared ammonium selenide. His product was a white, crystalline solid, which was readily decomposed by water in the presence of air. No mention occurs anywhere that this compound was ever obtained by crystallisation from solution, hence it may be of interest to note that when prepared by the latter method it crystallises in black, anhydrous, orthorhombic prisms. Peculiar conditions, however, seem necessary for its formation. Thus, in attempting to make ammonium selenomolybdate it was observed that when an ammoniacal solution of ammonium molybdate was saturated with hydrogen selenide gas a dark-red coloured solution resulted, which yielded the black crystals of ammonium selenide upon careful evaporation. The solution contained five grms. of ammonium molybdate in 50 c.c. of water, to which 20 c.c. of the strongest ammonia water had been added. The solution was saturated with hydrogen selenide gas. The resulting liquid, deep red in colour, was concentrated in a vacuum over sulphuric acid. The final residue consisted of ammonium molybdate, metallic selenium, and well-defined, black, orthorhombic crystals. The latter were separated as completely as possible from the selenium, and extracted for several days with pure carbon disulphide. The crystalline mass, purified as far as possible in this manner, proved to be stable in the air, and dissolved readily in water to a dark red coloured solution. The latter, when freshly made, precipitated selenides from neutral or alkaline solutions of metallic salts. On exposure to the air, however, the solution of the salt suffered decomposition with the separation of black selenium. An excess of ammonia seems not to prevent the change.

The analysis gave as follows:—

1. 0·3051 grm. of substance gave 0·2137 grm. selenium = 70·04 per cent selenium.

2. 0·2031 grm. of substance gave 0·1418 grm. of selenium = 69·81 per cent selenium.

Ammonium.

3. 0·2012 grm. of substance gave 0·0603 grm. of ammonium = 29·97 per cent ammonium.

4. 0·3036 grm. of substance gave 0·9918 grm. of ammonium = 30·24 per cent ammonium.

The discrepancy between the found and calculated percentages is due to metallic selenium, which adhered to the ammonium selenide crystals. The salt was distilled with sodium hydroxide in determining the ammonium content. The liberated ammonia was absorbed by standard hydrochloric acid, the excess of the latter being titrated with standardised alkali.

In estimating the selenium a weighed quantity of the salt was dissolved in water containing a little sodium hydroxide. An excess of hydroxylamine* hydrochloride was added to this solution, from which the selenium separated completely after boiling several minutes. It was then transferred to a weighed Gooch filter, washed with water, and dried at 105° for one hour. This method is far superior to the usual course of precipitating selenium by means of sulphurious acid.

The ammoniacal molybdate solution of the strength given in the preceding lines is the only solution from which the black crystals were obtained. Under these conditions the salt was always found, but with molybdate solutions of greater dilution or with such as contained arsenic acid or tungstic acid, evaporation showed nothing but metallic selenium.—*Journal of the American Chemical Society*, xx., No. 4.

SOME PROPERTIES OF ZIRCONIUM DIOXIDE.

By F. P. VENABLE and A. W. BELDEN.

There are so many misstatements as to the properties of zirconia in the literature of chemistry that we think it well to publish the results of our study of this body.

1. *Specific Gravity.*—The following values have been given:—4·30 (Berzelius), 4·90 (Berlin), 5·50 (Sjögren), and 5·45 (Hermann). Our determinations were made with quite pure material, and yielded as a mean 5·489.

2. *Solubility.*—The strongly ignited zirconia is practically insoluble in all acids except hydrofluoric. In this it is readily soluble on heating. If soda is present along with the zirconia, as sodium zirconate, the mass is not dissolved, probably owing to the formation of sodium zirconium fluoride. The statement is frequently met with that zirconia is soluble in sulphuric acid. This is based upon observations of Berzelius, and his directions are that the zirconia must be finely powdered and heated with a mixture of two parts sulphuric acid and one part water until the sulphuric acid volatilises. Our experiments would show that it is quite insoluble in concentrated sulphuric acid, and when the directions of Berzelius are followed out this dilute acid dissolves only 6·72 parts to the 1000 parts of acid. Neither concentrated nor dilute hydrochloric acid, nor nitric acid, seem to have much action upon it.

Prolonged heating with sodium carbonate effects very little change in zirconia. It is only sparingly dissolved. Berzelius must have made use of a carbonate carrying some hydroxide in the experiments in which he speaks of dissolving the zirconia by means of sodium carbonate.

Again, ½ a grm. of zirconia (finely powdered) was fused for nine hours with 20 grms. of microcosmic salt. The zirconia did not apparently enter into the fusion, nor could the formation of crystals be observed as has been maintained. The same results were observed in a similar experiment with borax.

3. *Zirconium Hydroxide.*—The statement is made in Dammer's "Handbook" (i., 619) that of the two possible hydroxides only $ZrO(OH)_2$ is known, and that, further, numerous pyrohydrates are known whose contents of water lie between this and the anhydride. This is based upon the work of G. J. Bruch (*Jahresber.*, 1854, 729), who described a meta-zirconic acid, $ZrO(OH)_2$, prepared as a white, voluminous, almost gelatinous precipitate, by precipitating a solution of a salt of zirconium with ammonia.

In the following experiments this precipitate, gotten with ammonium hydroxide, was washed free of ammonia, then placed in a Gooch crucible and washed about twelve times with alcohol (95 per cent). It was then washed with ether. After weighing the crucible it was heated strongly, and the loss of water was 26·50 per cent. In a second experiment the zirconium hydroxide precipitate was pressed between filter-paper, placed in a Gooch crucible, and washed with petroleum ether until there was no further loss of weight. This washing was done in an atmosphere free from carbon dioxide. Afterwards the crucible was strongly heated. The loss of water was 26·19 per cent. A third experiment carried out in a similar manner yielded also 26·30 per cent. Other experiments gave losses of 25·97 per cent and 27·21 per cent. The percentage of water in $Zr(OH)_4$ is 22·69. It would therefore seem that treatment with petroleum ether brought the precipitate very nearly down to the composition $Zr(OH)_4$. In using alcohol and ether there seemed to be no definite limit to the removal of water, and hence in several experiments final constant weights were not obtained. Two experiments gave respectively 11·11 and 9·45 per cent of water. The percentage in $ZrO(OH)_2$ is 12·80.

A specific gravity determination of the hydroxide containing 25·97 per cent of water gave 3·25.

4. *Solubility of the Hydroxide.*—The statement of Bruch, that this substance is soluble in 5000 parts of water, and turns litmus paper blue and turmeric paper orange yellow, is cited by several authors. This is manifestly an error. The alkaline reaction observed was doubtless due to the ammonia which it so persistently retains when ammonium hydroxide is used in the precipitation. Bailey and others have noted how prolonged the washings must be to free the hydroxide from ammonia. Experiments were carefully carried out to test this point, but we failed to detect in the pure hydroxide any alkaline reaction or any appreciable solubility in pure water. Certainly it is less than the figure given by Bruch.

The solubility of the cold precipitated hydroxide in acids is as follows:—It is very readily soluble in concentrated and dilute hydrochloric acid (which is the best solvent for it), in hydrofluoric acid, and in hydrobromic acid. It is very sparingly dissolved by hydriodic acid. Concentrated and dilute nitric acid dissolve it easily.

Among the organic acids it was found that oxalic acid was the best solvent, dissolving it nearly as well as the mineral acids. Saturated solutions of tartaric and citric acids dissolved less than 1 : 1,000 and glacial acetic acid also dissolved very little.

If the zirconium hydroxide is precipitated from a hot solution it is much less soluble in the dilute acids. Thus dilute hydrochloric or dilute nitric acid will dissolve only about 1 : 100 and dilute oxalic acid dissolves only about half as much. If the precipitate, however, stands for some days in contact with the acid it is dissolved to about the same extent as when precipitated cold.

As to the solubility in basic substances, ammonia (sp. gr. 0·90) does not seem to appreciably dissolve it, but when diluted (sp. gr. 0·96) there is dissolved about 1 : 10,000 parts of ammonia. Clarke (*Journ. Amer. Chem. Soc.*, xviii., 434), has shown the solubility in potassium hydroxide, and in sodium hydroxide to be as follows:—

	Grms.
50 per cent KOH solution dissolved per c.c. ..	0·00233
33 ,, ,, ,, ,, ,, ,, ..	0·00097
25 ,, ,, ,, ,, ,, ,, ..	0·00075
12 ,, ,, ,, ,, ,, ,, ..	0·00009
33 ,, ,, NaOH ,, ,, ,, ..	0·00245
25 ,, ,, ,, ,, ,, ,, ..	0·0012
12 ,, ,, ,, ,, ,, ,, ..	0·0005

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* Privately communicated by Dr. H. F. Keller.

Certain salts of ammonia exert quite a solvent action. Thus a saturated ammonium carbonate solution will dissolve about 1 : 100, and a solution of ammonium tartrate rendered strongly ammoniacal has a somewhat smaller solvent action.

5. *Absorption of Carbon Dioxide.*—Zirconium hydroxide shows a decided tendency to absorb carbon dioxide. This may be observed on exposing the moist precipitate to the air or on prolonged heating at a low temperature (100°—150°) over an ordinary burner. Such a mass will gain very noticeably in weight. The extent of this absorption of carbon dioxide was tested as follows: About two grms. of the moist hydroxide were placed in a porcelain boat in a tube and pure carbon dioxide passed over it for some twenty-five or thirty hours. At the end of this time the hydroxide had contracted into small, hard, horn-like particles and no further change was observable. Purified air was next passed over these particles for eighteen or twenty hours, and the carbon dioxide coming off was caught in a barium hydroxide solution and determined. Then the particles were heated and the carbon dioxide was caught by a fresh solution of barium hydroxide. It was found that about one-third of the carbon dioxide which had been absorbed came off without heating. As no distinct point could be observed at which this carbon dioxide ceased coming off (no clear line of demarcation between that lost at ordinary temperatures and that lost on heating), no inferences were drawn, and the carbon dioxide was all reported together. The percentages of carbon dioxide absorbed were 16·42, 5·72, and 7·05. These show a wide variation, and can scarcely be taken as showing more than the fact that considerable amounts of the gas are absorbed with the formation of basic carbonates. The basic carbonate, $Zr(CO_3)_2.2Zr(OH)_4$, contains 16·68 per cent of carbon dioxide, and $Zr(CO_3)_2.6Zr(OH)_4$ contains 7·55 per cent, and $Zr(CO_3)_2.8Zr(OH)_4$ contains 5·96 per cent.

This experiment was varied somewhat by suspending the zirconium hydroxide in water and passing carbon dioxide through the water. This gave 6·73 and 6·00 as the percentages of carbon dioxide absorbed in two separate trials.—*Journal of the American Chemical Society*, vol. xx., No. 4.

FURTHER SEPARATIONS OF ALUMINUM BY HYDROCHLORIC ACID.[*]

By FRANKE STUART HAVENS.

In former papers from this laboratory (Gooch and Havens, *Am. Journ. Sci.*, ii., 416; Havens, *Ibid.*, iv., p. 111), methods have been described for the separation of aluminum from ferric iron, and from beryllium, based on the insolubility of the hydrous aluminum chloride in a mixture of equal parts of aqueous hydrochloric acid and ether saturated with hydrochloric acid gas; the ferric and beryllium chlorides being exceedingly soluble in this mixture.

It was the purpose of the investigation herein described to discover how far this process could be extended, with certain modifications, to cover the separation of aluminum from such other metals as might occur with it, either in artificially prepared alloys or in naturally-occurring compounds.

The aluminum used in all the following experiments was in the form of a solution of the chloride. This chloride was purified, as previously described (*loc. cit.*), from iron by precipitation with hydrochloric acid, and from the alkalis by precipitation as the hydroxide and continued washing with water until the washings gave no test with silver nitrate. The hydroxide thus obtained was dissolved in hot hydrochloric acid to get it into the form of the chloride. The chloride solution was standardised by precipitating weighed portions with ammonia and weighing as the oxide.

Separation of Aluminum from Zinc.

A solution of pure zinc chloride made by dissolving metallic zinc, free from impurities, in hydrochloric acid, is not precipitated when treated with an equal volume of ether and saturated with hydrochloric acid gas.

To prepare a definite zinc salt free from traces of the alkalis which would be precipitated with the aluminum by strong hydrochloric acid, pure metallic zinc was dissolved in hydrochloric acid, the dilute solution precipitated with ammonium carbonate, and the resulting carbonate ignited to a constant weight as zinc oxide. This oxide dissolved in hydrochloric acid gave a pure chloride.

The aluminum in all these experiments was determined in the following manner:—Portions of the prepared solution of aluminum chloride were weighed in a small beaker, weighed portions of zinc oxide added and sufficient aqueous hydrochloric acid to dissolve it. The beaker was then cooled by immersion in an inverted bell-jar supplied with running water by means of inlet and outlet tubes, and a current of gaseous hydrochloric acid (generated by the gradual addition of sulphuric acid to a mixture of hydrochloric acid and salt) passed through the solution in the beaker to complete saturation. Ether was added in volume equal to that of the original solution, and the whole again saturated with hydrochloric acid gas. The crystalline chloride precipitated was caught on asbestos in a filter crucible, washed with a previously prepared solution of equal parts of ether and hydrochloric acid, saturated with hydrochloric acid gas, dried for half an hour at 150—180° C., covered with a layer of pure mercury oxide, heated gently over a low flame under a ventilating hood, ignited over the blast, and weighed as the oxide. The results show that aluminum can be determined with reasonable accuracy in the presence of a pure zinc salt.

The zinc can be determined, after the evaporation of the strong acid filtrate, by any of the well known methods. It was found, however, that after thorough conversion to the nitrate by repeated evaporation with nitric acid the salt could be ignited directly to the oxide with satisfactory results. This is shown clearly in Table I. (Experiments 3 to 5). In Experiments 3 and 4, zinc oxide was dissolved in nitric acid and the nitrate ignited again to the oxide. In Experiment 5, the zinc oxide was first dissolved in hydrochloric acid and the chloride thus obtained was converted to the nitrate by evaporating the solution (5 c.m.^{3}) with nitric acid (2 c.m.^{3}), treating the residue with nitric acid (2 c.m.^{3}), and evaporating to dryness.

In Table I. (Experiments 6—11) are given the results of experiments in which both the aluminum and zinc were determined—the former, as described, by precipitating as the hydrous chloride and weighing as the oxide, and the latter by carefully evaporating the strongly acid filtrate (best with a small current of air playing on the surface of the liquid to avoid spattering due to the too violent evolution of the ether and gaseous acid), and finally converting the chloride through the nitrate into the oxide. It is, of course, absolutely necessary that the treatment with nitric acid shall be thorough, so that no zinc chloride may remain to volatilise when the residue is ignited. On account of the danger to platinum from the aqua regia generated by the action of nitric acid on zinc chloride, the evaporations of the filtrates from the aluminum chloride and the treatment with nitric acid were carried on in porcelain, and the residual nitrate was transferred to a small crucible for ignition. In this process the porcelain was evidently attacked somewhat, so that the residual nitrate was slightly contaminated with material from the large porcelain dish. This fact accounts for the high results given in the first column of errors. However, on introducing a correction (0·0020) found by carrying

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[*] Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, vol. vi., 1898.

TABLE I.

	Al_2O_3 taken as the chloride. Grm.	Al_2O_3 found. Grm.	Error. Grm.	ZnO taken. Grm.	ZnO found. Grm.	Error. Grm.	Error corrected. Grm.	Final vol. C.m.^{3}.
1.	0·0562	0·0562	0·0000	0·1110	—	—	—	—
2.	0·0580	0·0577	0·0003 −	0·1034	—	—	—	—
3.	—	—	—	0·1019	0·1016	0·0003 −	—	—
4.	—	—	—	0·1010	0·1007	0·0003 −	—	—
5.	—	—	—	0·1100	0·1095	0·0005 −	—	—
6.	0·0572	0·0572	0·0000	0·1014	0·1027	0·0013 +	0·0007 −	12
7.	0·0563	0·0550	0·0013 −	0·1026	0·1038	0·0012 +	0·0008 −	16
8.	0·0577	0·0576	0·0001 −	0·1000	0·1014	0·0014 +	0·0006 −	16
9.	0·0559	0·0558	0·0001 −	0·1020	0·1035	0·0015 +	0·0005 −	16
10.	0·0563	0·0556	0·0007 −	0·2024	0·2046	0·0022 +	0·0002 +	20
11.	0·1111	0·1107	0·0004 −	0·2092	0·2116	0·0024 +	0·0004 +	20

TABLE II.

	Al_2O_3 taken as the chloride. Grm.	Al_2O_3 found. Grm.	Error. Grm.	CuO taken. Grm.	CuO found. Grm.	Error. Grm.	$HgCl_2$ taken. Grm.	Bi_2O_3 taken. Grm.
1.	0·0576	0·0571	0·0005 −	0·0500	—	—	—	—
2.	0·0561	0·0557	0·0004 −	0·0400	—	—	—	—
3.	0·0570	0·0574	0·0004 +	—	—	—	0·1000	—
4.	0·0548	0·0557	0·0009 +	—	—	—	0·1000	—
5.	0·0565	0·0571	0·0006 +	—	—	—	—	0·1000
6.	0·0576	0·0577	0·0001 +	—	—	—	—	0·2000
7.	—	—	—	0·0437	0·0432	0·0005 −	—	—
8.	—	—	—	0·0359	0·0359	0·0000	—	—
9.	—	—	—	0·0345	0·0340	0·0005 −	—	—
10.	0·0558	0·0545	0·0013 −	0·0319	0·0324	0·0005 +	—	—
11.	0·0538	0·0536	0·0002 −	0·0343	0·0356	0·0013 +	—	—
12.	0·0566	0·0562	0·0004 −	0·0337	0·0349	0·0012 +	—	—
13.	0·0577	0·0575	0·0002 −	0·0651	0·0644	0·0007 −	—	—

through the process in blank with the quantities of reagents employed in the regular process, the results on zinc, slightly deficient, agree closely with those obtained (Experiments 3—5, Table I.) where the zinc nitrate was converted directly to the oxide without the previous evaporation in porcelain of a large volume of strongly acid liquid. The errors thus corrected stand in another column of the table.

These results show clearly that aluminum and zinc may be separated from one another by the action of hydrochloric acid gas in aqueous ethereal solution with a reasonable degree of accuracy.

Separation of Aluminum from Copper, Mercury, and Bismuth.

The separation of aluminum from copper, mercury, and bismuth does not differ materially from the separation of aluminum and zinc. Aluminum chloride is precipitated quantitatively in the presence of pure salts of these elements, as shown in experiments of Table II.

In determining the copper in the acid filtrate it was found advantageous to weigh as the oxide, but to arrive at that condition through the sulphate rather than through the nitrate (which was the transition salt in the case of zinc), as this process can be carried on safely in platinum.

In Table II. (Experiments 10 to 13) are given results of experiments in which the aluminum was determined as previously described by precipitation as the hydrous chloride and conversion to the oxide, the acid filtrate was evaporated in platinum and the copper determined by treating the residue with a few drops of strong sulphuric acid, heating gently to drive off the excess of sulphuric acid, and then igniting the sulphate to the oxide at a red heat. That the copper sulphate is converted to the oxide by ignition at a red heat over a Bunsen burner is shown in Experiments 7 to 9 of Table II.

In conclusion, the author wishes to thank Professor Gooch, under whose direction this work has been carried on, for his kind suggestions and advice.

ACTION OF SULPHUR MONOCHLORIDE UPON MINERALS.

By EDGAR F. SMITH.

SULPHUR monochloride has frequently been applied in organic chemistry in the synthesis of various bodies, and the results obtained by the employment of this reagent have invariably had great attraction and interest for the investigator. There are, however, other directions in which the same reagent may be followed with equal interest; *e.g.*, in the action upon the natural products furnished by the mineral world. To illustrate, mention may be made of the behaviour of such substances as arsenopyrite, chalcopyrite, pyrite, and marcasite with the reagent in question. Finely divided arsenopyrite and sulphur monochloride were brought together in a glass tube. After slight agitation, action set in, accompanied by the evolution of much heat, and the almost complete decomposition of the mineral. The tube was then freed from air by the introduction of carbon dioxide. It was sealed and heated to about the boiling-point of the sulphur monochloride (139°) for a period of nine hours. On cooling, beautiful olive-green coloured plates or scales separated. After their removal from the tube and separation from the adherent liquid they proved to be deliquescent and readily soluble in water. Their aqueous solution tested with potassium ferrocyanide and silver nitrate showed the presence of iron in the ferric condition, and also of chlorine. In subsequent decompositions the crystals were filtered out, and washed with petroleum ether; then they were dissolved in water and the iron content determined quantitatively by means of stannous chloride. In this manner it was proved that 32·6 per cent of iron was present in the ferric condition in arsenopyrite. This is certainly a confirmation of the work previously carried out in this direction on arsenopyrite by Starke, Shock, and Smith (*Journ. Amer. Chem. Soc.*, xix., 948).

The petroleum ether solution from the ferric chloride crystals was distilled, the product diluted with water, and tested with hydrogen sulphide, when the arsenic was precipitated. Its quantity was not estimated.

Chalcopyrite treated in a similar manner with sulphur monochloride, was completely decomposed, with the production of ferric and cupric chlorides. Marcasite and pyrite also gave beautiful crystallisations of iron chloride. The decompositions were in both instances complete and the total iron content determined. On the addition of sulphur monochloride to marcasite and pyrite no action was observed in the cold. With chalcopyrite and arsenopyrite the evolution of heat, as already mentioned, was very great, so that the vessel containing them could not be held in the hand. This difference in behaviour evidently indicates a marked difference in the union of the elements concerned. In pyrite and marcasite we deal with iron and sulphur alone and with them there is an absence of marked reactivity, whereas in arsenopyrite and chalcopyrite we have substitution products in which there is perhaps a less intimate union of the sulphur than exists in the pyrite and marcasite. It may be observed here that Brown (*Proc. American Phil. Soc.*, xxxiii., 1894), while working with marcasite, found that it contained its total iron in the ferrous condition, but when this same mineral was dissolved in sulphur monochloride it gave a mass of iron chloride crystals showing the presence of about 41 per cent of iron in the ferric state. This would mean that this reagent undoubtedly acts as an oxidant; that its power is in a large measure due to its chlorine content, so that we may say of sulphur monochloride it is "chlorine in disguise." This view of its action is corroborated by other decompositions which will be presented later. The experiments upon which the preceding statements are based were carried out by Mr. F. W. Moore.

The mineral stibnite dissolved immediately and completely in sulphur monochloride with a violent ebullition and the generation of much heat. When the solution cooled crystals separated. These were collected and heated with water, with the formation of antimony oxychloride. Much heat was also evolved when cinnabarite and sulphur monochloride were mixed. To effect complete decomposition the mixture was heated in a sealed tube. On cooling long needles were observed throughout the liquid. These proved to be mercuric chloride. Chalcocite was also completely decomposed, with the production of a crystalline powder, which on examination was found to be cupric chloride. This is additional evidence of the oxidising character of the solvent employed, and explains the reason for the obtainment of so much ferric chloride when using marcasite, which contains its iron in the ferrous condition. Tetrahedrite, although of a complex nature, yields in the cold to the influence of the sulphur monochloride, and crystals of ferric chloride appeared in a very short time, although to effect the complete decomposition of the mineral it was necessary to heat it with the reagent to 140° C. Sphalerite was not attacked in the cold, and at 150° its decomposition was very slight, but at 250° C. complete solution occurred. On cooling, a mass of anhydrous zinc chloride separated. This was quickly collected and treated with water, when it dissolved with a hissing noise. The zinc in solution equalled 67·5 per cent.

Galenite, furthermore, was not affected in the cold, but at 250° C. was changed completely to lead chloride. Finely divided molybdenite was not attacked in the cold, nor was it entirely broken up after heating to 300° C. Many of these experiments show that, where the sulphur estimation of a sulphide is not desired, this method of decomposing such minerals may be of use in analysis. This is particularly true in the case of tetrahedrite. Mr. C. S. Reeve was kind enough to conduct these experiments for me.

At my suggestion, Mr. E. W. Pierce brought pure, artificial arsenic trisulphide in contact with sulphur monochloride. A violent reaction set in, and much heat was liberated. On repeating the experiment at a temperature of 0°, the reaction took place slowly with the gradual solution of the metallic sulphide and the appearance of a slight residue of sulphur, which disappeared on the addition of more sulphur monochloride. Nothing separated when the liquid was further chilled. Arsenic sulphide was precipitated from the diluted solution on the addition of hydrogen sulphide. The minerals linnæite $(Co,Ni)_3S_4$, millerite (NiS), gersdorffite ($NiAsS$), and rammelsbergite $(NiAs)_2$, were also fully decomposed by the monochloride on heating the mixture in sealed tubes to 170° C. Metallic chlorides were formed in all instances and separated from the cold solutions. Cobaltite ($CoAs$), smaltite ($Co(FeNi)As_2$), and ullmannite ($NiSbS$), in a finely divided condition, were dissolved by the sulphur monochloride when heated to 180° C. in a sealed tube. These observations were made by Mr. Jos. Cauffman, who also found that rutile in powdered form was decomposed almost completely by the same reagent, with the production of titanium tetrachloride. This behaviour suggested heating the oxides of molybdenum, tungsten, tantalum, and columbium, as well as the minerals wolframite, scheelite, and columbite with the same reagent when all were dissolved, and from the cold solutions beautiful crystalline bodies separated. Some of these have been analysed, while others are yet under examination and will be discussed in a later communication. The indications are that the action of the sulphur monochloride in these substances is both oxidising and substituting. Combinations of the metallic haloids with sulphur monochloride are not produced. In the case of the sulphides and sulpho salts which were investigated, quantitative determinations of the products were only made in a few instances, for there was no question as to the completeness of the decompositions, and the character of the resulting bodies. Upon considering the facts which are here presented, we recognise that with the sulphides of non-metals, for example stibnite, the action is violent, and the decomposition complete. This is also true of arsenopyrite where arsenic probably facilitates the transposition, whereas with marcasite, pyrite, sphalerite, galenite, &c., the reaction is more sluggish. From an examination of the excess of sulphur monochloride in these different experiments it would seem that the original sulphur of the mineral is merely dissolved out, for upon evaporation it separates in large quantities.—*Journal of the American Chemical Society*, vol. xx., No 4.

SOME PRINCIPLES AND METHODS OF ANALYSIS APPLIED TO SILICATE ROCKS.*

By W. F. HILLEBRAND.

(Continued from p. 45).

THE foregoing tables and accompanying remarks, including several sentences preceding the tables, have been largely taken from the writer's paper entitled "A Plea for Greater Completeness in Chemical Rock Analysis," published in the *Journal of the American Chemical Society* (vol. xvi., pp, 90—93, 1894), also in the CHEMICAL NEWS (vol. lxix., p. 163, 1894).

Scope of the present Paper.

The literature relating to analysis of silicates is extensive, but scattered; and the scheme given by Fresenius in his "Qualitative Analysis" answers well for the ordinary separations, and is probably almost universally followed in all its essential features; but in no single article, to the writer's knowledge, is there to be found an exposition of the methods to be followed, or the precautions to be observed in the search for some of the

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* From the *Bulletin of the United States Geological Survey*, No. 148, p. 15, 1897.

rarer constituents or those which, without being rare, have been of late years recognised as occurring persistently in small amounts. It is not the object of the writer to make this paper a treatise on mineral analysis; but it is believed that the experience gained by the chemists of this Survey during the sixteen years since the establishment of its first chemical laboratory in Denver may be useful to most chemists interested in mineral and especially rock analysis. Lengthy descriptions of details of manipulation will be avoided so far as possible, and in general only an outline will be presented of the methods followed or recommended, since in the main they are familiar to all or easily accessible; but stress will be laid on those points meriting particular attention, and now and then a brief discussion of alternative methods may be attempted.

In the earlier years of the existence of the Washington laboratory opportunity was afforded for the testing of novel methods and the devising of new ones, with most excellent results, as shown especially by the methods for separation of titanium, of lithium, and of boron, due to Prof. F. A. Gooch, to whose inventive skill chemists owe likewise the perforated filtering crucible and the tubulated platinum crucible arrangement for the estimation of water. Of late years the press of routine work has been such as to fully fill up the time of the much-reduced chemical force, and as a consequence it has been found impossible to subject to critical trial several separation methods of recent origin, some of which seem to be full of promise, or to follow out certain lines of investigation which have been suggested by the observations made in this laboratory, one, at least of which, seems to be of high importance. This, then, must be offered in explanation, if, in the following discussion, it may seem to some that any of the methods followed are too conservative or not sufficiently up to date. In general the discussion will be confined strictly to such separations as may be required in the analysis of an igneous, metamorphic, or sedimentary silicate rock of complex mineralogical composition, in which the majority of, and possibly all, the ingredients in the list given below may occur in weighable or readily discoverable quantities:—

SiO_2 TiO_2 ZrO_2 Al_2O_3 Cr_2O_3 Fe_2O_3 FeO
NiO CoO CuO MnO CaO SrO BaO
MgO K_2O Na_2O Li_2O H_2O CO_2 C†
SO_3 S* N Fl Cl

* Usually as pyrite, not infrequently as pyrrhotite.
† As graphite or coaly matter.

The special problems often arising in the analysis of rocks of extra-terrestrial origin—the more or less stony meteorites—will not be considered in this paper. An analysis of that kind should never be entrusted to the novice, but only to the chemist who has a knowledge of the composition and properties of the peculiar mineral constituents of those bodies, and a judgment fit to cope with the oftentimes difficult problems presented by them.

Thorium, cerium, and other rare earths are seldom encountered in quantities sufficient to warrant the expenditure of the time necessary for their isolation. A search for them qualitatively, even, is at present rarely justifiable unless there is microscopic or other evidence of the presence of minerals likely to contain them. Vanadium, tantalum, columbium, boron, and glucinum have never been certainly met with in the writer's experience, and yet they must be present in certain rocks, and doubtless traces have been overlooked at times. There is no reason to suppose that other elements may not be found by careful search, possibly all in the known category, and, indeed, Sandberger's researches have shown to what an extent this is true of a large number of those elements contributing to the filling of metalliferous veins. But those in the above list may usually be estimated with ease in weights of from one-half to 2 grms.

If the point be raised that many of the published analyses emanating from the Survey laboratories, even the earlier ones of the writer, are not in accord with the advocacy of completeness contained in the foregoing pages, it may be remarked that these ideas have been to a considerable degree evolved during a personal experience of sixteen years in this line of work, and that frequently the exigencies were such as to compel restriction in the examination. Where the latter has been the case subsequent developments have in some cases shown it to be bad policy in every respect. It is better, both for the geologist and the chemist, to turn out a limited amount of thorough work than a great deal of what may prove to be of more than doubtful utility in the end.

In this connection the question has often been put, "How long does it take to complete an analysis of this kind?" This will depend, of course, on the mineral complexity of the sample and on the personal factor of the individual worker. If there is a competent assistant to do the grinding, and specific gravity determinations are not required, it is quite possible after long experience for a quick worker to learn to so economise every moment of time in a working day of seven hours, with an abundance of platinum utensils and continuous use of air- and water-baths through the night, as to finish every three days, after the completion of the first analysis, barring accidents and delays, one of a series of rocks of generally similar character, each containing from eighteen to twenty quantitatively determinable constituents, excluding, for instance, fluorine, carbon as such, nitrogen, metals of the hydrogen sulphide group, and cobalt. On one occasion a series of fourteen rocks, of comparatively simple composition, was completed in one month, with the help of an assistant who made the phosphorus and ferrous iron determinations. But such an output of work is more than exceptional, and implies an unusual freedom from those occasional set-backs to which every chemist is exposed.

PART II.—*Discussion of Methods.*

Preparation of Sample.

Although foreign to the above heading, a few words relative to the sample itself may be here appropriately inserted by way of introduction. In the great majority of cases a few chips from a hand specimen will well represent the average of the mass, but with rocks in which a porphyritic structure is strongly developed the case is different. Here a large sample should be provided, gauged according to the size of the crystals, and the whole of this should be crushed and quartered down for the final sample. Unless this is done it is manifest that the analysis may represent anything but the true average composition of the rock.

Crushing.—Mechanical appliances for reducing samples to fine powder are much in use in technical laboratories, where they answer their purpose more or less admirably, and something similar is needed in those scientific laboratories where rock analysis is of daily occurrence and many samples must be reduced to fine powder in a short space of time. For accurate analyses the use of steel crushers and mortars is out of the question, because of the danger of contamination by particles of metal and the impossibility of cleansing the roughened surfaces after they have been in use a short time. Extraction of steel particles from the powder by aid of a magnet is quite inadmissible, since the rocks themselves, almost without exception, contain magnetic minerals. The method of rough crushing found to be most satisfactory in practice is to place each fragment as received on a hardened steel plate about 4½ c.m. thick and 10 c.m. square, on which is likewise placed a steel ring 2 c.m. high and of about 6 c.m. inner diameter, to prevent undue flying of fragments when broken by a hardened hammer. In this way a considerable sample can soon be sufficiently reduced for transfer to the agate grinding mortar with a minimum of metallic contamination.

Grinding.—Of the various grinding arrangements on the market purporting to fulfil their purpose, few, if any, observed have met the conditions required by the work in hand. Either the mechanical arrangement is complicated or cumbersome, requiring more power or space than is usually at disposal, or causing too much noise, or thorough cleansing is difficult and troublesome, or there is likelihood of contamination from oil or grease, or lack of facility for the removal of all powder from the mortar. These last defects are especially prominent in those forms in which the mortar is fixed in its setting.

All rock samples have therefore been reduced to powder by hand, involving a great expenditure of time and labour. Ordinarily an extremely fine state of division is unnecessary, except in the case of those portions in which alkalies and ferrous iron are to be estimated, or where soluble constituents are to be removed by acids, &c., and in such cases the final grinding can be done at the balance table on a small portion slightly in excess of the quantity to be weighed off.

The process of sifting through fine cloth, the German "beuteln," is one not always to be commended, because of the time required, and, more especially, because of the certainty of contamination by cloth fibre, which in the ferrous-iron portion might affect the result. Still less should metal sieves be used.

Weight of Ground Sample.—The sample when ground should weigh not less than 10 grms, and preferably 20, in case it should be necessary to repeat or advisable to employ unusually large portions for certain determinations, notably carbonic acid. Rock analysis has in this respect an advantage over mineral analysis, since material is almost always available in ample quantity and any desired number of separate portions may be used, whereas with a mineral the analyst is frequently compelled to determine many or all constituents in a single, often very small, portion of the powder. This course often involves delay and the employment of more complicated methods of separation than are usually necessary in rock analysis.

Specific Gravity.

By Suspension in Water.—This determination, when required, is best made upon one or several fragments weighing up to 20 grms. They are held together by a fine platinum wire ready for suspension from the balance, and thus held are placed in a small beaker to soak overnight in distilled water under the exhausted receiver of an air-pump, side by side with a similar beaker of water. Boiling is of course a much less effective means of removing air than the air-pump, and the boiling water may exert an undesirable solvent and abrading effect. In the morning the wire is attached to the balance arm, the rock fragments remaining immersed in the water; a thermometer is placed in the companion beaker of water, now likewise in the balance case, and the weight is at once taken. Both vessels of water having precisely the same temperature, it is quite unnecessary to wait for the water to assume that of the balance should it not already possess it. The fragments are now lifted out, without touching the vessel, and carefully transferred to a tared crucible or dish; the wire is removed, and at once re-weighed, with the precaution that it dips just as far into the water now as when weighted. Hereby a special weighing of the wire out of water is avoided. The sample may now be dried on the water-bath, and then at 110° C. for some hours, to certainly expel all absorbed water, and weighed after prolonged cooling in the desiccator. It is better to ascertain the weight of the dry rock after soaking in water than before, in order to avoid the error due to possible breaking off of a few grains between the two weighings. Should the density of the rock in air-dry condition be required,* it may be left exposed to the air for a lengthy period after drying and before weighing; but the difference will only in exceptional cases affect the second decimal by more than a single unit. For instance, a rock of 2·79 specific gravity when dry will, if carrying the high percentage of 0·3 per cent hygroscopic moisture in the uncrushed state, have a density of 2·775; a rock of 3·00 specific gravity dry will have a density of 2·982 if 0·3 per cent of moisture is included.

Reasons for preferring Suspension to Pycnometer Methods.—This method of ascertaining the specific gravity of rocks is certainly more convenient than, and for compact rocks is believed to be decidedly preferable to, that of the pycnometer, in which the fragments must be reduced to small size with consequent formation of more or less powder, which is subject to slight loss in the various manipulations. To exclude this powder and employ only small fragments would introduce a possible source of error, since it is apt to consist largely of the most easily abraded minerals, and consequently not to have the average composition of the mass. By following the instructions given above, loss of material is absolutely avoided, a decided saving in time is effected, and considerable weights can be easily employed with consequent lower probable error in the results. To vesicular rocks, however, notably certain lavas, the above procedure is of course inapplicable, unless the datum is desired for certain considerations in which the relative density of large rock masses as they occur in Nature is sought, as for the comparison of building stones or the calculation of large known or assumed areas of particular rocks.

Pycnometer Methods.—If the pycnometer has to be used, as is generally the case when the density of any one of the mineral ingredients of a rock is desired after separation by one of the approved methods, it being then in a more or less finely divided state, the most accurate procedure is that adopted in this laboratory by Mr. L. G. Eakins a number of years ago. The pycnometer used is one with a capillary stopper, provided with a millimetre scale etched in the glass, the divisions being numbered both ways from the centre and calibrated by mercury, so that the value of each one in weights of water is known. The capacity of the flask filled with water to the zero division is then calculated for every half degree of temperature from 0° C. to 30° C., by making a series of careful weighings, in which, knowing the capacity of the stem, it is quite immaterial at what level the water stands provided it is within the limits of the scale. The exact temperature is secured by an accurate thermometer placed in a companion vessel of similar shape to the pycnometer and containing a like amount of water, both being left in the balance case till its temperature has been nearly or quite assumed, as shown by a second thermometer. The weighing must of course be made before the thread of water has sunk beneath the lowest division, which it will do after a time, even though at first filling the bore to the top of the stopper; and the corrected weight full of water to the zero mark is found by adding or subtracting the needed amount, as shown by the height of the thread on the scale.

For each pycnometer in use, and these are of different sizes, is prepared a table showing its weight, the value of each scale division in grms. of water, and the capacity of the flask at different temperatures, as indicated above. The preparation of such a series of flasks is time saved in the end, for the weighing of the flask full of water each time a density determination is made is rendered superfluous. All that is necessary is to look up in the table the weight corresponding to the temperature.

The density of the previously weighed substance in this case is now determined in much the same way, after the unstoppered pycnometer containing it, and nearly

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* In view of the uncertainty as to what constitutes hygroscopic water, this course is perhaps more to be commended than the former, and seems imperative for certain zeolitic rocks. In such cases it is best to weigh the fragments before putting to soak, and afterward to collect on a Gooch crucible the grains which may have fallen off in the water. Should no crucible of this kind be available, a paper filter may unhesitatingly be used and incinerated with the powder, owing to the small amount of which the error due to loss o even all its water during ignition is quite negligible.

filled with water, has stood with its companion vessel of water under the air-pump the necessary length of time. The water needed to fill the flask is taken from its companion.

All who have used the pycnometer method for fine substances know the difficulty experienced in preventing a portion from being held at the surface, despite all attempts at making it sink. Hence it often happens that a very small portion runs out around the sides of the stopper on inserting it. If the flask rests in a small tared dish the grains thus forced out may be washed down into it and weighed after evaporation, in order to get the correct weight of that in the flask; or, after weighing, the contents of the flask may be emptied into a tared dish, and the water slowly evaporated off in order to get the weight of the mineral. Usually this way is less to be recommended than the other.

Penfield's Method for Mineral Fragments.—Penfield (*Am. Jour. Sci.*, 3rd Series, vol. l., p. 448, 1895) recommends the following modification of the suspension method as more convenient than that by the pycnometer in many cases for small fragments of minerals:—

After boiling in water, the substance is transferred with water to a small glass tube about 8 m.m. by 35 m.m., provided with a fine platinum wire for suspension. This is weighed full of water in another vessel of water, and again after the removal of the mineral, the weight of which is found after drying.

This method is, of course, more applicable to homogeneous minerals than to rock fragments, and will therefore be applied in rock analysis chiefly to the determination of the specific gravity of the mineral grains separated by heavy solutions or acids.

Heavy Solutions not available in case of Rocks.—Because of their roughness, porosity, and complex mineral composition, the density of rock fragments cannot be accurately determined by that of heavy solutions in which they may remain suspended.

Weights of Sample to be employed for Analysis.

With only occasional exceptions nearly all the constituents mentioned on page 56 can be estimated, if present, in 1 grm. of rock sample. This is a convenient weight to take for the main portion in which silica, alumina, &c., the alkaline earths, and magnesia are to be sought; but it should in general be a maximum, because if larger the precipitate of alumina, &c., is apt to be unwieldy. Its weight cannot often be much reduced with safety if satisfactory determinations of manganese, nickel, and strontium are to be expected. For the alkali portion one-half grm. is a very convenient weight. In general it may be made a rule not to use more than 2 grms. for any portion which has to be fused with an alkaline carbonate, as for sulphur, fluorine, chlorine. For carbon dioxide the weight may rise to 5 grms. or even more, if the amount of this constituent is very small, without expenditure of any more time than is required by 1 grm., and with correspondingly greater approach to correctness in the result.

(To be continued).

ELECTROLYTIC DETERMINATIONS.

By EDGAR F. SMITH and DANIEL L. WALLACE.

1. *Uranium.*

SOME years ago one of us found that it was possible to completely precipitate uranium (*Am. Chem. J.*, i. 329; Smith's "Electrochemical Analysis," p. 94) from an acetate solution by means of the electric current. The deposit consisted of the hydrated protosesquioxide of uranium, which was ignited and weighed as U_3O_8. Indeed, the procedure was adopted in the separation of uranium from the alkali metals when they were associated in certain rare minerals. It has frequently been used since that time by the author, and its reliability has been fully confirmed. However, Heidenreich (*Ber. d. Chem. Ges* xxix., 1587) evidently experienced some difficulty in obtaining satisfactory results, for he remarks:—"Versuche, Uran aus seiner Acetatlösung quantitativ abzuscheiden führten zu keinem Ergebniss, selbst bei 50-stündiger Einwirkung des elektrischen Stromes." A method requiring fifty hours would scarcely be regarded as having value, even if the final results were really good. The following experiments, however, show that not only can satisfactory results be obtained, but they furthermore leave little doubt as to the time-factor, which is of prime importance in all determinations.

A solution of uranium acetate was prepared, which contained 0·1185 grm. of urano-uranic oxide (U_3O_8) in 10 c.c. of the liquid. To the latter volume were added 5/10ths c.c. of concentrated acetic acid, and the whole was then diluted to 40 c.c. with water, when it was electrolysed with a current N. $D_{40}=0·18$ A. V=3. The temperature of the liquid during the decomposition was 70° C. The uranium was completely precipitated in six hours. The filtrate or solution poured from the deposit showed no traces of uranium, when it was evaporated and the residue tested for that metal.

Results.

U_3O_8 present in grms.	U_3O_8 found in grms.
0·1185	0·1187
0·1185	0·1184
0·1185	0·1182

2. *Cadmium.*

Those interested in electrolysis will probably remember that the writers have at various times proposed methods and conditions not only for the electrolytic determination of this metal, but also for its separation from the more frequent associates. So often have we ourselves carried out these separations that we were inclined to believe other chemists would meet with like success. Such, however, seems not to have been the case, for in a very recent issue (*Journ. Amer. Chem. Soc.*, xix., 870) we felt called upon to publish very carefully outlined conditions for the complete deposition of cadmium from acetic and nitric acid solutions in order to again confirm our early statements. Heidenreich (*Ber. d. Chem. Ges.*, xxix., 1587) mentions that the separation of cadmium from solutions containing sodium phosphate and free phosphoric acid gave results which were "ebenfalls nicht quantitativ; die letzten Reste von Kadmium sind nicht zu entfernen, selbst wenn der Strom bis 1-Ampère verstärkt wird." We regret exceedingly that this chemist has met with so little success in his efforts to repeat our work, but, as in former instances of disagreement, we again present new experimental evidence showing that our original suggestions were undoubtedly correct.

To 10 c.c. of a cadmium sulphate solution, containing 0·1656 grm. of metallic cadmium, were added an excess of disodium hydrogen phosphate (1·0358 sp. gr.) and 1½ c.c. of phosphoric acid (1·347 sp. gr.). The liquid was then diluted to 100 c.c., heated to 50° C., and electrolysed with a current N. $D_{100}=0·06$ A. Volt=3. The precipitation was finished in seven hours. The metal deposits were bright and adherent. They did not show the slightest trace of sponginess. At the expiration of four hours the current was increased to N. $D_{100}=0·35$ A. Volt=7. The acid liquid was syphoned out without the interruption of the current. The pole separation, during the entire precipitation, equalled 1½ inches. The cadmium was washed with hot water and then carefully dried. The filtrates were examined, but did not reveal a trace of unprecipitated metal. This is a direct contradiction of Heidenreich's statement that "die letzten Reste von Kadmium sind nicht zu entfernen."

Results.

Cadmium present in grms.	Cadmium found in grms.
0·1656	0·1654
0·1656	0·1658
0·1656	0·1657

—*Journal of the American Chemical Society*, xx., No. 4.

CORRESPONDENCE.

THE YEARLY INDEX TO "THE JOURNAL OF THE CHEMICAL SOCIETY."

To the Editor of the Chemical News.

Sir,—I fully sympathise with your correspondent "A Fellow of the Chemical Society" in his complaint of the long delay in the publication of the index to the *Journal of the Chemical Society* for 1897. I have never had the opportunity of knowing anything of the internal working of the Society, but, speaking as an outsider, it appears to be inexcusable that we should be well into July and the index for the previous year still remain unpublished. If the work were performed in the manner which common sense appears to indicate, the index would be ready for the printer immediately the December number of the journal was issued. I presume the members of the Council of the Chemical Society do not *use* the journal, or their self-interest would soon put a stop to the discreditable delay attending the publication of the index.—I am, &c.,

A Fellow of Thirty Years' Standing.

July 26th, 1898.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Zeitschrift für Physikalische Chemie, Vol. xxv., No. 8.

Estimation of Dissociation Constants by Increase of Solubility.—Richard Lowenherz.—The author has limited himself to the proof of the fact that the dissociation constant can be calculated from experiments on solubility, and a few examples of the practical methods used for this calculation. He uses the bases aniline and *p*-toluidine of various concentrations, and the two acids cinnamic and *p*-nitrobenzoic. A number of small flasks, containing 250 c.c. of solution, are placed in a water-bath. The water used for solution must be distilled and freed from CO_2. In order to get the solutions quite saturated at the temperature of the experiment (25°), the solution is first raised to 35°, well shaken, and then allowed to remain at 25° for some hours. The liquid is filtered and titrated with 1/100 N baryta water, phenolphthalein being used as an indicator. The acids for the experiments are purified by being many times re-crystallised from water, and the bases by being boiled with lime and distilled.

Simultanous Application of the Law of Mass Action and the Phase Rule.—K. Kuriloff.—Unsuitable for abstraction.

The Variation with the Temperature of the number of Nuclei which are formed in Different Supercooled Liquids.—G. Tammann.—The author makes experiments on a large number of organic substances, and the chief conclusions he draws are:—(1) The number of points from which crystallisation can start in a super-cooled liquid is excessively small in comparison with the number of molecules present. (2) The number of points increase with strong super-cooling until a maximum is reached, and then they decrease in a fairly symmetrical manner. (3). Foreign substances, whether soluble or insoluble, affect the number of nuclei. (4) The temperature of maximum nucleus formation is very slightly changed by the addition of a small quantity of the substance.

Investigations on the Influence of Mediums on the Reaction Velocity in Gaseous Systems.—Ernst Cohen.—Menschutkin and Carrara showed that the velocity with which a given reaction takes place is affected to a high degree by the character of the medium. The author extends this series of experiments to ascertain in how much the reaction velocity of gases varies when the same reaction takes place in various chemically indifferent mediums. He uses for his experiments AsH_3, obtained by the decomposition of pure As_2Zn_3 by dilute boiling H_2SO_4, in atmospheres of H, N, CO_2, &c. His experiments prove that the decomposition velocity of AsH_3 at 310° is not influenced by the presence of H or N, which result is in accordance with Nernl's theory.

Measurement of Electrical Conductivity in Dilute Solutions at a Temperature of about 100°.—R. Schalle.—The author shows, by means of experiment with a large number of organic and inorganic acids and their sodium salts, that the conditions of the electrodes exercise a great influence on the measurement of the conductivity of dilute solutions. The electrodes have previously to be boiled for some time with water, and in order to avoid the error as much as possible it is better to use small electrodes which are platinised, a little lead acetate having been added to the platinising solution. Vessels of Jena glass are used, as they practically resist the action of neutral salts and acids, when very dilute at 99°. The influence of the glass can be taken as constant, if measurements of it are taken with water. The following results are obtained:—(1) All electrolytes, when completely dissociated, increase their conductivity when the temperature is raised, the curve being linear. (2) The conductivity of acids which are not completely dissociated diminish with increase of temperature.

Combination and Substitution.—F. Wald.—Unsuitable for abstraction.

The Internal Friction of Electrical Solutions.—Hans Euler.—The author finds (1) that the internal friction of electrolytes depends on the friction of the ions and the undissociated portions, according to the equation $H = S^x A^y K^y$, where S = friction constant of the undissociated parts, x = its concentration; A and K = the friction constants of the anion and kathion respectively, y = their concentration. (2) There is a quantitative relation between the friction coefficient of the elementary ions and the migration velocity.

The Equilibrium Systems: Water, Ether, and Succinic Acid Nitrite.—F. A. H. Schreinemakers.—Unsuitable for abstraction.

Zeitschrift fur Analytische Chemie, Vol. xxxvii., No. 3.

Estimation of Sugar in Sweet Wine and Polarimetric Investigations. — Arthur Bornträger. — The author refers to a former paper in which he describes the preparation of sweet wine simultaneously for polarimetric experiments and estimation of sugar. He repeats the treatment to prove the accuracy of the results, and also examines the effect of varying proportions of sugar and alcohol on the polarimetric observations.

Researches on Masut.—N. Kromer.—By the term "masut" is meant the residue left from the refining of petroleum oil. This substance is used in Russia for burning purposes. Specimens of this were examined, taken from various places, and all were found to have a black colour, a more or less viscous consistency, and an acid reaction. The portions taken for distillation were dried over calcium chloride. The distillation took place in an Engler's flask, and the boiling-points were noted; also the temperatures at which the oil burns spontaneously, which was very low in some of the specimens.

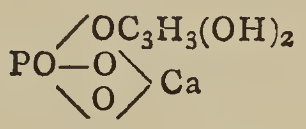
White Soda Lime.—Cl. Lageman.—The author has succeeded in preparing soda lime perfectly white, which he says can be prepared as cheaply as the ordinary grey substance.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xix.-xx., No. 7.

Action of Chloride of Aluminium on Anhydrous Chloral. — A. Mouneyrat. — 882 grms. of anhydrous chloral were placed in a dry flask of 1500 c.c. capacity, the flask was kept cool by means of iced water, and 167 grms. of finely-powdered, perfectly anhydrous, chloride of aluminium were gradually added, keeping the flask constantly agitated; after standing a few moments the mass becomes solid. The flask is then fitted with a vertical condenser, and heated on a water-bath; a regular stream of hydrochloric acid is given off; when this ceases, the still warm liquid is run into iced water slightly acidulated with HCl, and violently shaken; torrents of hydrochloric acid gas came off. A thick, heavy, brownish oil falls to the bottom, and after decanting and drying it is distilled fractionally; finally, at 120—121°, a small quantity of perchlorised ethylene ($CCl_2 = CCl_2$) is obtained, at 159—160° a considerable quantity of pentachlorethane, and above 160° a thick heavy oil with a strong choking odour.

Chloridation of Sulphide of Carbon in the presence of Chloride of Aluminium. — A. Mouneyrat. — In view of the powerful chloridising action of chloride of aluminium in the fatty series, the author wished to decide whether sulphide of carbon, chloridised in the presence of this powerful synthetic agent, would behave like iodine; he found that such was not the case, as the sulphide of carbon passes entirely to the state of tetrachloride before the sulphur can pass to the state of chloride, SCl_2.

Phosphoglycerate of Lime, and the Estimation of Neutral Phosphoglycerates.—MM. Adrian and Trillat. —The analysis of well-dried phosphoglycerate of lime, as obtained by the authors, gave:—Phosphoric acid, 32·93 per cent; lime 26 per cent, being very close to the formula—



$$PO\begin{cases}OC_3H_3(OH)_2\\ O\\ O\end{cases}\!\!\!\!>Ca$$

If we add sulphuric acid of a known strength to a cold aqueous solution of a neutral phosphoglycerate, using heliantine as an indicator, the change appears the moment we have added half a molecule of acid for one molecule of the neutral salt: from this reaction a very rapid method of estimating neutral phosphoglycerates has been devised.

Contribution to the Study of the Reaction of Phosphoric Acid on Glycerin.—MM. Adrian and Trillat.— The observations made by the authors show that there is not yet a method known for obtaining phosphoglyceric acid in the pure state,—that the acid is decomposed by heat, and even by concentration *in vacuo*, re-forming phosphoric acid.

On Hydrocinnamide. — Marcel Delépine. — Hydrocinnamide, $C_{27}H_{24}N_2$, results from the union of cinnamic aldehyd, C_9H_8O, and ammonia, with elimination of water. Dehydrated hydrocinnamide dissolves easily in benzene, but separates out in impure yellow crystals, melting at 131°. Its heat of formation is −79·4 cal. (cryst.).

Synthesis of Terebic Acid.—E. E. Blaise.—Already inserted.

Camphoric Acid.—G. Blanc.

Constitution of Camphoric Acid.—G. Blanc.—These two papers are too long for useful abstraction, but the author claims to have proved that M. Bouveault's formula will explain all the facts yet known on the subject.

Two Coloured Reactions of Pyruvic Acid. — L. Simon. — If potash is first added to pyruvic acid, $CH_3—CO—COOH$, and then nitro-prussiate of soda, a beautiful intense violet-red colour is produced; by this means 1 part of pyruvic acid in 50,000 can be detected. If ammonia be added first, and then the nitro-prussiate of soda, a beautiful violet-blue colour appears after the lapse of a few minutes, but the limit of sensitivenes is only about 1 in 10,000.

A Coloured Reaction of Ordinary Aldehyd. — L. Simon.—Already inserted.

A New Coloured Reaction of Phenylhydrazin.— L. Simon.—Already inserted.

Thermic Study of Azelaic Acid.—G. Massol.—The quantity of heat given off by azelaic acid is less than that obtained with its normal homologues, even with those which have a fairly high molecular weight; it is +41·53 cal., suberic acid being 44·76 cal., and sebacic acid 43·09 cal.

Research on the presence of Hydrocyanic Acid in various Plants.—A. Hébert.—The author finds that hydrocyanic acid in plants does not occur in sufficiently large quantities to be protective. Certain Japanese plants which contain a comparatively large quantity are only seriously toxic in doses of 300 to 400 grms. Many others, containing a normal quantity, would require several kilos. to be ingested for any harm to be done.

MISCELLANEOUS.

West Ham Technical Institute.—The Council of the County Borough of West Ham have made the following appointments on the teaching staff of their new Technical Institute:—Lecturer in Physics and Mathematics: Mr S. G. Starling, B.Sc., A.R.C.Sc. (Lond.), of the Battersea Polytechnic. Assistant in the Art Department: Mr. Mervyn Lawrence. Demonstrator in Physics: Mr. J. Tomkin, A.R.C.Sc., of the Royal College of Science. Demonstrator in Chemistry: Mr. F. H. Streatfeild, of Finsbury Technical College.

Institute of Chemistry of Great Britain and Ireland.—July Examinations, 1898.—Examiners: Professor Percy F. Frankland, F.R.S., F.I.C.; Otto Hehner, F.I.C.

Names of Candidates who Passed the Practical Examination for the Associateship (under Regulations in force prior to October 1st, 1893).—John Bristowe Pease Harrison, Yorkshire College, Leeds, and Registered Student under Thomas Fairley, F.I.C.; *Harold Nolan, M.B. (Lond.), Guy's Hospital and the British Institute of Preventive Medicine; *George Egerton Scott-Smith, Assistant to A. H. Allen, F.I.C.

Intermediate Examination (New Regulations).—Robert Duncombe Abell, University College, Bangor; William Arthur Cates, Finsbury Technical College; Walter Thomas Collis, Mason University College, Birmingham; Alexander Davidson, jun., William Smith Denham, and James Faill, Glasgow and West of Scotland Technical College.

Final Examination for the Associateship (New Regulations).—In Branch "A" (General Inorganic Chemistry): Leonard Myddelton Nash, King's College, London. In Branch "B" (Metallurgical Chemistry): *Frederic William Daw, Assoc. R.C.Sc. (Lond.), Royal College of Science, London. In Branch "D" (Organic Chemistry): Harry Thornton Calvert, B.Sc. (Vict.), Yorkshire College, Leeds; Robert Howson Pickard, B.Sc. (Lond.), Ph.D. (Munich), Mason University College, Birmingham. In Branch "E" (The Analysis of Food and Drugs, and of Water): Alexander Nash Crosskey, A.C.G.I., Central Technical College, London, and under J. Kear Colwell, F.I.C.; *Edward Russell, Charing Cross Hospital and St. Mary's Hospital. (Those marked with an asterisk for the Fellowship).

NOTES AND QUERIES.

Separation of Molybdenum.—Would some reader give a few references to reliable methods of *quantitatively* separating molybdenum from large amounts of iron. Processes dealing fully with the estimation of molybdenum in iron alloys would be especially valuable. References to English journals preferred —H. B.

THE CHEMICAL NEWS.

Vol. LXXVIII., No. 2019.

ON THE YTTRIC EARTHS FROM THE MONAZITE SANDS.

By G. URBAIN.

I have already announced the results of my first researches on the fractionation of the ethylsulphates of the earths of the yttric group. My later researches on the same subject have only confirmed and completed the former. This method is especially suitable for separating these complex mixtures into groups of the bodies to which the already-described methods are best applicable. The inevitable presence of intermediate portions is principally due to the fact that the component parts of raw ytrria do not separate one from the other in an equally distinct manner. If it is an easy matter to obtain solutions containing erbium, perfectly free from holmium, it is extremely difficult to completely eliminate the erbium from the fractions rich in holmium. In the same manner if the earths of the terbia group are easily separated at first, the yttria present will be found in all the fractions.

The existence, previously pointed out, of a lower limit of fractionation of an atomic weight of about 97 has entirely to do with the difficulty experienced in separating yttrium from small quantities of the terbia earths. The greater part of these earths is generally precipitated by potassic sulphate, when we try to eliminate, by the aid of this reagent, the last traces of didymium kept in solution by the yttria earths, in such a manner that the yttria always remains contaminated with a certain quantity of the earths of the terbia group; this mixture, with an atomic weight of about 97, shows a remarkable persistence.

MM. Schutzenberger and Boudouard were the first to call the attention of the Academy to this limit of fractionation, but without having determined its exact nature.

I have admitted in a previous note that it contains principally yttrium, and I have since solved the problem in a complete manner, by isolating from this material yttria having an atomic weight of 89 and some earths of the terbia group of which the atomic weight reaches as high as 151·4, a figure which may still be below finality.

In the series of fractionations of the ethylsulphates which contain only yttrium, true erbium, and ytterbium, I was easily enabled to isolate yttrium with an atomic weight of about 89, by precipitations with ammonia. These fortunate results were due to the absence of the terbia earths. From this it appeared to be probable that by numerous crystallisations of the *heads* of the fractionations of the ethylsulphates (initial atomic weight 97) the terbias, if present in this material, would accumulate in the first crystals, in the same manner as was done by the didymium in the preceding fractionations.

Experiment fully confirmed these anticipations. After a sufficient number of crystallisations, the different fractions, transformed into oxides, gave tints varying from deep orange (*heads*) to those of a pale rose colour (*tails*). These last retained a small amount of erbia, which was removed by crystallising the oxalates in nitric acid; the last mother-liquors from these fractionations were yttrium having an atomic weight of 89.

The coloured oxides belonging to the terbia group were characterised by the slight solubility of their formates. At any rate on being calcined in hydrogen they lost a scarcely sensible fraction of their weights.

They were transformed into a nitrate glass, and examined spectroscopically by reflection. I have only been able to detect two bands in the visible part of the spectrum.

Micrometer.	λ		
70	0·000	Hardly seen.	Holmium.
122—130	0·000	Intense.	Dysprosium.

These different characters suffice to show that this body is still complex in character; but the experiments prove that the yttria from the monazite sands contains principally yttrium with an atomic weight of 89, and that there does not exist an element whose atomic weight would be about 97 or 100.—*Comptes Rendus*, vol. cxxvii., No. 2, July 11, 1898.

ON THE HEAT OF FORMATION OF CARBIDE OF LITHIUM.

By M. GUNTZ.

To determine the heat of formation of this compound it suffices to measure the heat given off by the solution in water of a known weight of carbide of lithium; in this manner I have found that at about 17°—

C_2Li_2 sol. + nH_2O liq. = $2LiOH$ diss. + C_2H_2
Disengaged gas .. .. + 37·10 cals.

This figure is the mean of three experiments which gave + 36·65, + 37·27, and + 37·25.

In order to do away with the correction due to the solubility of acetylene in the colorimetric liquid, the decomposition was effected in a glass apparatus plunged into the colorimeter: C_2H_2 was freely given off into the air. On each occasion the actual amount of the carbide used was verified by titration. In two of the experiments we took note of the free carbon, in the third we had pure carbide.

These data sufficed to calculate the heat of formation of carbide of lithium, knowing at the same time the heat of solution in water of lithium.

I thus found—

C_2 (diamond) + Li_2 sol. = C_2Li_2 sol. .. +11·3 cals.

This is certainly a high number; it is much greater than the corresponding values found for CaC_2 and NaC_2; but it explains the easy formation of this compound under diverse circumstances.

To prepare Li_2C_2, I heat metallic lithium with carbon, but many precautions must be taken in order to ensure success.

In a glazed porcelain tube another tube of combustion glass was placed, and in this second tube was the iron boat containing the mixture of carbon and lithium (as a rule these two substances were present in equal proportions by weight). The porcelain tube was then firmly stoppered, the apparatus exhausted and then brought to a dull red heat for about half-an-hour.

If we make use of sugar charcoal for the carbon, even when strongly calcined, combination with incandescence takes place when operating on 2 or 3 grms. of lithium, on account of the formation of LiH; acetylene prepared by means of this compound always contains traces of hydrogen. Carbide of lithium is also produced, but without incandescence, when we use carbon which has been heated in the electric arc, or graphite. It is also formed by using diamond.

To prove this fact I heated, in vacuo, in a glass tube and an iron boat, a few fragments of cut diamonds; it is afterwards seen by examining the fragments of diamond under the microscope that the polish has disappeared by reason of the erosion which is characteristic of the reaction.

In the preparation of carbide of lithium it is necessary to use a double tube, because without this precaution the vapour of lithium attacks the porcelain tube, and in nearly every case causes a breakage; a vacuum is necessary, for at a red heat lithium absorbs all gases except argon. The tube must not be brought to a bright red heat, because in vacuo the carbide of lithium dissociates too rapidly into carbon and lithium, in fact the dissociation even begins at a dull red heat.

By operating in the foregoing manner we obtain a greyish mass, sometimes coloured slightly yellow by iron; this is the carbide of lithium we wish to obtain. If it is heated for too long a time it will be contaminated by carbon. I have not been able to obtain this compound by the method which enabled M. Matignon to prepare pure carbide of sodium, on account of the readiness of melted lithium to attack glass, nor by M. Moissan's method as I had not sufficient electrical energy at my disposal.

By heating electrically 1 or 2 grms. of a mixture of $C_2+Li_2CO_3$, as described by M. Moissan, I always happened to entirely volatilise the whole of the carbonate of lithia, without obtaining a trace of carbide of lithium, which seems to indicate that a temperature high enough to volatilise Li_2CO_3 was still not sufficient to dissociate it into its elements and give free lithium, a condition necessary for obtaining the carbide.

Carbide of lithium possesses one very interesting property; when it is heated with melted chloride of lithium, or the fusible mixture $LiCl+KCL$, it decomposes, giving Li_2Cl and carbon; but at a high temperature Li_2Cl dissociates, giving $LiCl+Li$.

Lithium attacks the carbon set at liberty to reform the carbide; there is, therefore, an equilibrium formed at a high temperature, the reaction being reversible. This explains why we cannot make use of a carbon rod for the negative pole for the purpose of electrolysing LiCl, because at the temperature of electrolysis the lithium formed attacks the carbon and gives a carbide, which, by diffusing through the mass of the chloride, decomposes and gives carbon, which remaining in suspension in the liquid, impedes any useful formation of lithium.—*Comptes Rendus*, vol. cxxvi., No. 26, June 27, 1898.

ON THE LIMITS OF INFLAMMABILITY OF COMBUSTIBLE GASES.

By H. Le CHATELIER and O. BOUDOUARD.

The inflammability of gaseous mixtures is a most complex problem,—it must of necessity depend on most varying conditions, such as the heat of combustion, the speed of combination, &c. The work already done in this direction—unfortunately too little—has not formulated any precise relationships between the different phenomena which come into play. If we wish to sufficiently multiply the number of the experiments we must not confine ourselves to the combustible gases only, but we must include combustible vapours, which comprise a large number of compounds met with in organic chemistry.

To determine the limit of inflammability of a vapour—that is to say, the smallest quantity of this vapour which, when mixed with a definite quantity of air, is inflammable—we must not follow the same method as in the case of a gas. We have, in the case of very volatile liquids, such as ether, sulphide of carbon, and benzene, introduced successively known weights of these bodies into a flask of 2 litres capacity, previously full of air. A stirring apparatus, already in the flask, served to assist the evaporation, and also to render the mixture homogeneous.

The experiment was repeated until we obtained two separate weights, varying by at least 10 per cent, the weakest of which gave an uninflammable mixture and the strongest an inflammable one. The mean of these two numbers was taken as the limit of inflammability, which is thus within 5 per cent of the true figure.

In the case of slightly volatile bodies, such as the alcohols, essence of turpentine, or naphthalene, we should place the body in a 500 c.c. flask, kept at a constant temperature. A thermometer, to which a stirrer is attached, accelerates the saturation of the air. The temperature, corresponding to the limit of inflammability, has been determined to within 1 degree. To estimate the quantity of vapour existing in the mixture at this temperature, we passed a known volume of air (2 litres) through a small tube containing pumice-stone saturated with the liquid, and kept at the same temperature. The loss of weight gives the quantity of liquid which must be vapourised in order to furnish a volume of the mixture equal to 2 litres augmented by the volume of this vapour.

This method is, however, less exact than the preceding one, for two reasons :—On the one hand, the rapid variations in the vapour tension due to alterations of temperature; and on the other hand, by reason of the difficulty of perfectly saturating a given mass of air. The experimental errors by this second method may be at least twice as great as those by the first.

In the Table in which the results are collated, the letters at the heads of the columns have the following significance:—

t. Saturation temperature of the air.
p. Weight of vapour, per litre of the mixture, at a temperature of 15°.
v. Volume of vapour in 100 volumes of the mixture.
o. Volume of oxygen necessary for the complete combustion of the vapour.
q. Quantity of heat given off by the combustion of 1 molecular volume of the mixture,—that is to say, 23·5 litres at 15°.

The figures in modern type show the actual results of experiments; the others are calculated from these results by the known relations between the molecular weights and the heats of combustion.

	t.	*p*.	*v*.	*o*.	*q*.
Compounds experimented on.	Degrees.	Grms.			
Hydrogen	—	—	10	5	6·9
Carbonic oxide	—	—	16	8	11
Sulphide of carbon	—	0·063	1·94	5·9	4·9
Coal gas	—	—	8·1	9	10
Petroleum ether	—	0·045	—	—	13
Essence of petroleum	—	0·051	—	—	13
Petroleum oil	46·5	0·057	—	—	14·5
Methane	—	—	6	12	12·9
Pentane	—	0·034	1·1	9	9·5
Hexane	—	0·048	1·3	12·7	13·1
Heptane	—	0·047	1·1	12·3	12·9
Octane	—	0·049	1·0	12·6	13·1
Nonane	12	0·045	0·83	11·6	12·1
Acetylene	—	—	2·8	7	8·9
Amylene	—	0·046	1·6	11·9	12·8
Benzene	—	0·044	1·5	11	11·6
Toluene	—	0·049	1·3	11·4	11·8
Turpentine	30·5	0·042	0·73	10·2	10·9
Naphthalene	69	—	—	—	—
Acetone	—	0·073	2·9	11·6	12·7
Methyl alcohol	8	0·081	6	9	10·8
Ethyl do.	13·5	0·060	3·07	9·2	10·3
Propyl do.	25	0·065	2·55	11·5	12·5
Isopropyl do.	17	0·068	2·65	12	12·7
Isobutylic do.	27·5	0·053	1·68	10·1	10·8
Allylic do.	25	0·074	3·04	12·5	13·4
Amylic do.	38	0·045	1·19	9·0	9·5
Acetic acid	36	0·103	4·05	8·1	8·9
Ethylic oxide	—	0·060	1·9	11·7	12·5
Ethylic acetate	—	0·087	2·3	11·7	12·3
Nitrate of ethyl	—	0·145	3·8	—	12·2

Putting aside hydrogen and sulphide of carbon, of which the inflammabilities are very great, it will be noticed that for all the other bodies examined the heat of combustion of the mixture taken on 1 molecular volume is comprised between 9 cals. and 13 cals., and that that for most of them is between 12 cals. and 13 cals.; numbers which do not vary more than the possible errors of experiment. We are therefore warranted in stating, in a general manner, that the limit of inflammability of the greater part of the carbon compounds corresponds to a heat of combustion of about 12·5 cals. The same table shows that the amount of oxygen consumed in the combination of these mixtures also varies very slightly from 11·5 of the total volume of the mixture.—*Comptes Rendus*, vol, cxxvi., No, 21.

LABORATORY NOTES.

By HORACE JERVIS.

Bottle Labels.

In a previous communication (Chem. News, lxxvii., 133) a solution of sealing wax is recommended for labelling bottles. Instead of lettering with a stiff brush, we find that a piece of glass tubing drawn out at one end is easier to use, and gives the letters a beaded appearance. When the solution is partially evaporated and somewhat thicker, a rubber tube joining the pen and the lips enables the sealing-wax to be forced out as required. In this way one can letter as quickly as with pen and ink.

The wax is not brittle when dry, and thus supplies a very durable as well as tasty means of lettering and numbering the backs of note-books. It may be used also for such purposes as waxing the $CaCl_2$ tubes of Geissler potash bulbs where heating tends to fracture the ground-glass joint. Such articles should then be dried in a water-oven.

Silicon in Steels.

Dudley's announcement that in steel analysis the dehydrated silica is re-dissolved, if allowed to stand after diluting, was reproduced in various journals (Chem. News, lxx., 186), without specifying that it referred particularly to Drown's process, in which the dehydration is affected with hot H_2SO_4. On this account the operators of various methods have scrupled to avail themselves of the convenience that a delay at such a point sometimes affords.

There are a number of methods in which the iron salts are evaporated to dryness, and the silica dehydrated by baking. Samples treated so might safely await the more convenient season in this baked state if it were not that, long after they have cooled, they sometimes fracture the bottom of the beaker. If, however, they be taken straight from the hot plate, and a stream of *hot* water be delivered round the inside of the beaker, this cracking is avoided, and, as we have satisfied ourselves experimentally, they may stand for days without error. This refers more particularly to a method in which the steel is dissolved in a mixture of sulphuric acid (125), nitric acid (208), and water (500).

Quantitative Estimation of Phosphorus in Phosphides.—Léon Franck.—During his researches on the compounds of aluminium with phosphorus, the author found considerable difficulty in estimating the phosphorus, owing to the fact that aluminium phosphides are very unstable in air. He has since devised a method which gives very accurate results. It depends on the oxidation of the evolved PH_3 by means of bromine, and the estimation of the phosphoric acid formed. A drawing is given of the apparatus. The phosphide is contained in a vessel connected with three tubes containing a saturated rolution of bromine in hydrochloric acid. Dilute sulphuric acid is dropped, from a dropping funnel, on to the phosphide, and the evolved gas passed into the bromine solution. The vessel containing the phosphide is connected with a Kipp's apparatus, evolving CO_2, by which the air is first driven out and afterwards the PH_3 into the bromine solution. The phosphoric acid in the three tubes is estimated in the usual way.—*Zeit. Anal. Chem.*, xxxvii., No. 3.

SOME PRINCIPLES AND METHODS OF ANALYSIS APPLIED TO SILICATE ROCKS.*

By W. F. HILLEBRAND.

(Continued from p. 58).

Water—Hygroscopic.

Importance of not Drying before Weighing.—The time-honoured custom of drying a powdered specimen before bottling and weighing has long seemed to the writer one that has no sound basis in reason. Its object is of course plain, namely, that of securing a uniform hygroscopic condition as a basis for convenient comparison of analytical results, since some rocks contain more hygroscopic moisture than others. Nothing, however, is more certain than that by the time the substance is weighed it has re-absorbed a certain amount of moisture, small, indeed, in most cases, but very appreciable in others; and further, with every opening of the tube moisture-laden air enters, and is enclosed with the remainder of the dry powder. It therefore may very well happen that a powder at first dry will, after several openings of the tube, especially at considerable intervals, be nearly as moist as when first enclosed.

It is preferable to weigh the air-dry powder, and to make a special determination of moisture at 100° or 110° C. If all the portions necessary for an analysis are weighed out one after another, or even at different times on the same day, the error due to difference of hygroscopicity in dry and moist weather, which for most of the separate portions is an entirely negligible quantity, is eliminated. Only in the main portion, in which silica and the majority of the bases are to be estimated, can it ever be an appreciable factor.

Temperature of Drying.—As to the temperature to be adopted for drying in order to determine so-called hygroscopic moisture, the practice has varied at different times and with different workers, ranging from 100° to 110° C. For the great majority of rock specimens it is quite immaterial which of these temperatures is adopted, since no greater loss is experienced at the higher than at the lower temperature, given a sufficient time for the latter. Since the drying is accomplished more rapidly at 110° than at 100°, it is the present practice in this laboratory to employ the higher temperature. Should the results show a very unusually high loss, the powder is re-heated at, say, 125°, in order to learn if the loss is progressive with increased temperature. In the affirmative case it may be well to repeat the drying at 100°, for a portion of the loss at 110° was probably due to combined water from a mineral or minerals in the rock; but in that case even the loss at 100° may sometimes very well include combined water, and a further drying over sulphuric acid alone may be desirable, or over dry sand.

Cautionary Hints.—In this latter connection it is proper to point out certain pitfalls in the path of the unwary, which, however, are far more apt to be encountered in the analysis of minerals, where their influence may be of far-reaching consequence.

A mineral which loses a great deal of water over sulphuric acid—2 or 3 per cent, for instance—may need an exposure of several days or even weeks for its complete extraction. If the weighings are made from day to day, the apparent limit may be reached long before all water really removable has been taken up by the acid. Whenever the crucible, after weighing, is replaced in the desiccator, it is no longer in a dry—but a more or less moist—atmosphere, and its contents, even when covered, sometimes absorb a part of this moisture, and retain it so persistently that the acid is unable to bring the powder beyond its previous state of dryness in the next twenty-four hours. In fact, it may be unable even to reach it

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* From the *Bulletin of the United States Geological Survey*, No. 148, p. 15, 1897.

unless greater time is allowed. An experiment on 1 grm. of tyrolite, made and published some years ago, seems to illustrate this point in part:—

Hours exposed.	Loss. Grm.
18	0·0231
26	0·0083
23	0·0029
24	0·0012
23	0·0008
24	0·0001
25	0·0003
24	0·0002
24	0·0003
48	0·0006
24	0·0002
283	0·0380

The experiment might reasonably have been considered ended after the 158th hour, when a loss of but 0·1 m.grm. was shown during twenty-four hours; but nevertheless a nearly steady loss of 0·3 m.grm. per day took place for six days more, and might have been longer observed but for the interruption of the experiment.

Again, it is sometimes desirable to determine the water given off by hydrous minerals in an air-bath at temperatures far above 100° C. To ensure accuracy this experiment should not be made in crucibles or dishes which must be cooled in a desiccator. One instance will suffice:—A grm. of a mineral mixture containing about 17 per cent of water, of which about 3 per cent was driven off at 100° and 8 or 9 per cent at 280°, was, after several hours' heating, placed in a desiccator over sulphuric acid and weighed as soon as cold, then replaced and again weighed the next day. It had gained 1½ per cent of its original weight, although the desiccator was tightly closed and the crucible covered, showing apparently a drying power superior to that of the acid.

A specimen of tyrolite was found on one occasion to lose 10·34 per cent at 280° C., and on another occasion 14·33 per cent. In the latter case the drying and heating at progressive temperatures had continued during a period of 528 hours, the weighings being made usually from day to day; whereas in the former the duration of the experiment was much shorter, and the intervals between weighings were but a few hours each.

Procedure in Special Cases.—For experiments of this nature the powder should be heated in a weighed tube, through which a current of dry air can be passed, and allowed to cool therein, or else the water given off should be collected and directly weighed in suitable absorption-tubes,* even though the long time often required is an objection to this latter method, since the absorption-tube may gain weight, other than that of the water from the mineral, sufficient to introduce an appreciable error.

The recent important research of Friedel (*Bull. Soc. Min.*, vol. xix., pp. 14, 94, 1896; *Comptes Rendus*, cxxii., p. 1006, 1896) well shows what errors are possible in the determination of this easily removable water, since he found that certain zeolites which had been largely dehydrated but not heated to the point of rupture of the molecular net, could then absorb, instead of water, various dry gases in which they might be placed,—as carbon dioxide, ammonia, carbon disulphide, and others, even air in large quantities, and certain liquids. In the light of this observation, the cause of the great increase of 1½ per cent in weight of the partially dehydrated mineral mentioned above may very possibly be attributed to air from the desiccator instead of moisture, as was at the time supposed. At any rate, as Friedel says, the danger of accepting a loss in weight as an index of the amount of water lost is clearly shown, and thus that method of determining water is for many cases fully discredited. Just what method to adopt must be largely left to the judgment of the operator, who will often be guided by the mineral composition of the rock as revealed by the unaided eye or the microscope.

Friedel (*loc. cit.*) indicates a means for determining the true weight of water lost by minerals behaving like the zeolites, even without collecting the water lost, namely, by driving out of the dehydrated and weighed mineral, under proper precautions, any air it may have absorbed in the process of drying and cooling, and collecting and measuring this air and thus finding its weight, which, added to the apparent loss, gives the true contents in water.

Argument in favour of including Hygroscopic Water in Summation.—The question has been asked:—"If the so-called hygroscopic water is not always such, but not infrequently includes combined water, why is not its determination and separate entry in the analysis entirely unnecessary? Why make a distinction which, after all, may not be a true one?" The question involves the further consideration of the advisability of including in the analysis at all the loss at 100° or 110° C. Many petrographers desire to have all analyses referred to a moisture-free basis, in order that they shall be strictly comparable, and therefore would omit the "hygroscopic" water from the list of constituents. This would be eminently proper were it always possible to be sure that the loss at 100° truly represents mechanically held water. Since it very often represents more, and the determination as to whether or not it does in each case is not always possible, and would add to the time required for the analysis, it seems necessary to include this water. What errors may arise from its exclusion the following rather extreme case well illustrates:—Certain rocks of Wyoming in powder form lost from 1 to 2 per cent of moisture at 110°. That not even an appreciable fraction of this was truly hygroscopic the fact of the uncrushed rocks losing the same amount fully demonstrates; yet the rule followed by many chemists and petrographers would have involved the removal of all this water as a preliminary to beginning the analysis, and not only would a most important characteristic have passed unnoticed, but the analyst would have reported an incorrect analysis, inviting to false conclusions and possibly serious confusion.

Separate Entry of Hygroscopic and Combined Water.—To revert now to the primary question, it may be said that the estimation of the loss at 100° or 110° C., and its separate entry in the analysis, is advisable as not infrequently affording at once to the lithologist an indication of the mineral character of one or more of the rock constituents, thus perhaps confirming the microscopical evidence or suggesting further examination in that line. An unusually high loss at 100° would be regarded as probable evidence of the presence of zeolites or other minerals carrying loosely combined water. It has been objected that the true hygroscopic moisture varies with the degree of comminution of the sample and with the condition of the air at the time of weighing, and that it is therefore improper to incorporate it in the analysis; but this variation is ordinarily not at all great. Perhaps the time may come when it will be the rule to ascertain by additional heating at a higher temperature whether the water lost at 100° is to be regarded as purely hygroscopic. In such case it would be proper to omit it, and a distinct advance would undoubtedly be scored.

Is all true Hygroscopic Water expelled at 100°?—It has been tacitly assumed in the foregoing that true hygroscopic water can all be expelled at 100°, which perhaps is not to be accepted as universally true. Eminent authority holds that it is impossible, in the cases of certain foliaceous minerals, notably the micas, to thus entirely remove it, but that a part is only driven off at higher temperatures. If this is true a further uncertainty is introduced in its determination, which not only strengthens the argument

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* Jannasch and Locke (*Zeitsch. für Anorg. Chemie*, vol. vi., p. 174, 1894) describe and depict a form of apparatus adapted for either method of ascertaining hygroscopic water.

in favour of entering all water in the tabulation, but also serves to emphasise the difficulties of the situation.

Water—Total or Combined.

Arguments against "Loss on Ignition" Method.—In a few cases the simple loss on ignition of a rock will give the total water with accuracy, but in the great majority there are so many possible sources of error that this old-time method can rarely be used with safety. Only when the rock is free from fluorine, chlorine, sulphur, carbon, carbon dioxide, and fixed oxidisable constituents, can the loss be accepted as the true index of the amount of water present, and it is rarely that a rock is met with fulfilling these conditions, especially as to the absence of ferrous iron. Blast ignition in presence of carbon dioxide alone of the above list may give a correct result, after separate estimation of the carbon dioxide, provided this emanates from carbonates of the earths and not from those of iron or manganese. The long-maintained and still upheld idea, that in presence of ferrous iron a sufficiently correct result is obtainable by adding to the observed loss an amount needed for oxidising all ferrous iron, is not justifiable. There can be no certainty that the oxidation has been complete, especially in the case of readily fusible rocks, and at the high temperature of the blast a partial *reduction* of higher oxides is not only possible but sometimes certain. The inability to insure complete oxidation by simple ignition is illustrated in the case of precipitated ferric hydroxide, which has been ignited together with its filter-paper. If the quantity was in any degree large it is sometimes decidedly magnetic, presumably from presence of magnetic oxide, which no amount of heating wholly oxidises, especially in the larger grains.

Brush and Penfield's Method.—Direct weighing of the water evolved is, then, imperative in most cases, and, if no other volatile constituents are present, the beautifully simple method first used by Prof. G. J. Brush and extended by Prof. S. L. Penfield (*Am. Jour. Sci.*, 3rd Series, vol. xlviii., p. 31, 1894; *Zeitsch. für Anorg. Chemie*, vii., p. 22, 1894), leaves nothing to be desired for accuracy. It consists simply in heating the powder in a narrow tube of hard glass, enlarged at the closed end and provided with one or two further enlargements in the middle to hold the water and prevent its running back and cracking the hot glass. A capillary glass stopper, fitted in with rubber tubing, prevents the loss of water by circulating air currents. The tube being held horizontally, the bulb is heated to any required degree, either in the blast alone or the simple combination of blast with charcoal backing used by Penfield, which gives the white heat requisite for complete expulsion of water in some cases. Moistened filter-paper or cloth wound about the cooler parts of the tube insures condensation of all water. The heated end being finally pulled off, the tube is weighed after cooling and external cleansing, and again after the water has been sucked out by aspiration. For most rocks, as they contain little water, central enlargements of the tube are hardly needed.

How this simple apparatus is made to afford entirely satisfactory results, even when carbonates are present, is fully set forth in the paper cited.

Few rocks, comparatively, are altogether free from other volatile constituents; hence for refined work the application of this apparatus in the simple manner above set forth is limited. It may, however, be used with the addition of a retainer for fluorine, sulphur, &c., in the shape of calcium, lead, or bismuth oxides, or even with sodium carbonate.

In whichever way used the water found is the total water, from which that found separately at 110° C. may be deducted if desired.

Gooch's Apparatus.—Of more elaborate apparatus designed to be used with fluxes the tubulated platinum crucible invented by Dr. Gooch (*Am. Chem. Jour.*, ii., p. 247, 1880) is capable of affording most excellent service, and it is the one by which far the larger number of water determinations in this laboratory have been made. Since its manner of use is probably not generally known, some directions may not be amiss. A detailed description of the apparatus itself would not be clear without a figure; but it may be said that the form now used differs from that figured in Gooch's paper and his subsequent slight modification of it, in that the tubes for connecting with both the drying and absorption vessels are constructed wholly of platinum instead of lead glass, the vertical one being bent horizontally at right angles for convenient attachment to the drying towers, and the side one also bent at right angles, but downward, so as to admit of insertion in the rubber stopper of a U-shaped calcium chloride tube. The length of the vertical tube, including its horizontal part from top of cap, is 13½ c.m.; that of the side tube is 12 c.m. The end of the latter is drawn in slightly, so as to enter the rubber stopper of the absorption tube without scraping it. With tubes of the lengths above given there is absolutely no danger of their ends becoming hot enough by conduction to scorch or soften the rubber stopper or other connection.

The extra first cost of the platinum extension to these tubes over the lead-glass ends of Gooch's original and modified forms need hardly enter as a factor in the question of employment of this apparatus. The glass ends often break, and only a rich lead glass—not easily obtainable—can be used, since it alone will not crack at the joint with the platinum after cooling. In its present form the whole apparatus weighs approximately 88 grms.

As an adjunct to its convenient use there is needed an ordinary upright iron ring-stand, with one small sliding ring, and above this a sliding ring-burner provided with entering ducts for gas and air-blast. Still above this is another small ring, across which there is an arrangement of stout platinum wire, forming at the centre of the ring a secure seat for the upturned flange of the crucible proper. Both rings and burner can be clamped firmly at any height.

The rock powder, having been placed in the cylindrical crucible, is there mixed with not more than 3 or 4 grms. of fully dehydrated sodium carbonate,* or more of lead chromate if carbon is to be likewise determined, the crucible is sunk in its seat in the upper ring, and the tubulated cap is fitted on and attached to the calcium chloride drying towers on the one side, and to a sulphuric acid bulb tube on the other. Powdered sodium tungstate—free from arsenic, which would soon ruin the crucible lips—is now poured into the flanged lip in which the cap rests, and a metal vessel of cold water having been raised up by the lower ring until the platinum crucible is sufficiently immersed, the blast-fed flame of the ring-burner, or that of an ordinary blast-lamp, if at hand, is turned on to melt the tungstate. As soon as this is fused the flame is removed, and the salt solidifies and makes an air-tight joint, the test of which is the permanence of the column of sulphuric acid in the bulb tubes caused by the contraction of the air in the platinum apparatus as it cools.

After drying by a current of air at 110° C. for a couple of hours, more or less (see below), the absorption tube is interposed between the sulphuric acid bulbs and the apparatus, being fitted to the latter by its stopper, which is at other times closed by a glass plug, and while a slow current of air continues to pass the gradual heating and subsequent fusion of the flux is brought about by the blast-fed sliding ring-burner. When fusion is complete, as shown in the case of sodium-carbonate flux by the decided slackening of the gas current through the safety bulbs attached to the drying tube, the flame is extinguished and a current of air is allowed to continue until the apparatus is cold.

This apparatus suffers from the drawback of being slightly permeable to combustion gases at high temperature. The defect can be overcome by causing the flame

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* This has been heated for a length of time to near its fusing-point over a free flame or in an air-bath, to decompose the bicarbonate it usually contains, and then placed in a desiccator.

to play upon an outer ordinary platinum crucible, kept permanently filled with sodium-potassium carbonate. This protective crucible, however, is soon ruined for other purposes, being distorted by the alternate expansion and contraction of the carbonate.

It has been found that if the operation is carried out expeditiously, and the final full heat applied for but a few minutes, the error due to penetrating water gases is inappreciable. This hastening may be rendered safer by using rather finely-powdered calcium chloride in the central section of the U-shaped absorption tube to avoid large air channels. Through this, or any apparatus based on similar principles, the air current should always be forced, not drawn. A warm blast directed upon the exit tube near its entrance into the absorption tube greatly shortens the time required, and is to be recommended.

In this apparatus only the water expelled above 100° to 110° should as a rule be determined, and to effect drying of the mixed mineral powder and sodium carbonate, after luting the tubulated cap on the cylindrical crucible with sodium tungstate, the tube is sunk through a round hole in the cover into a small cylindrical air-bath, which can be heated from beneath by the same ring-burner which is subsequently to fuse the flux. A slow current of air is then forced through and the drying satisfactorily accomplished.

The reason why it is unsafe to attempt estimation of "hygroscopic" moisture in this apparatus is, that the luting of the two parts must be done by direct application of a flame to the tungstate, and considerable water vapour may enter the apparatus and be in part retained by the dried sodium carbonate.

Chatard's Apparatus.—The platinum apparatus devised by Dr. Chatard (*Am. Chem. Journ.*, xiii., p. 110, 1891; *Bull. U.S. Geol. Survey*, No. 78, p. 84, 1891) overcomes the permeability of the metal to gases, and affords sharp results, moreover permitting of determining by direct absorption not only the hygroscopic water, but that which may be driven off at any desired temperature. It is, however, more costly than the Gooch apparatus, and the supposed non-liability to injury by warping, because of the protective layer of borax and asbestos, can hardly be considered as proved.

Penfield's Second Method.—Simplest of all, and permitting by the use of auxiliary arrangements such as shown in Chatard's paper of determining the hygroscopic as well as any other fraction of the water, is the glass tube arrangement described on page 37 of Dr. Penfield's article cited on page 65.

All of these apparatus, except the first-mentioned glass tube, permit of the estimation of other constituents besides water in the same portion if necessary, and by the use of lead chromate or potassium chromate instead of sodium carbonate, graphite, or the carbon of organic matter, can be simultaneously determined with the water.

To one accustomed to its use, and with a drying and suspension attachment permanently set up, the Gooch apparatus, considering its limitations above set forth, offers perhaps the most handy and convenient means for the determination of water in rocks. Its high first cost, in comparison with the glass tube, is fully made up in time by its durability.

Jannasch's Methods.—That most zealous deviser of improved methods in mineral analysis, Prof. P. Jannasch, has published, in the *Zeitsch. fur Anorg. Chemie* and the *Ber. Deutsch. Chem. Gesell.*, several papers dealing with the problem of water determination in minerals besides the one already cited. Beginning with lead oxide as a flux, he subsequently experimented with lead chromate, borax, and boric acid, finding all of these to give accurate results in most cases when his directions are carefully followed, but unfortunately not capable (with the exception, perhaps, of lead chromate), like sodium carbonate, of general applicability, since with certain minerals one or the other fails to effect complete decomposition or to retain all volatile constituents. Especially for these reasons, also because the methods have not been tested in this laboratory and because Prof. Jannasch is still engaged in extending the boric-acid method, their use is not at present advocated for rock analysis. Moreover, the rock must be in such an impalpable powder for the boric-acid decomposition that a half to one hour has to be expended in the grinding of 1 grm. or less — a serious consideration for the busy chemist.

(To be continued).

THE DETERMINATION OF SMALL QUANTITIES OF ALCOHOL.*

By FRANCIS G. BENEDICT and R. S. NORRIS.

THE methods for the determination of alcohol ordinarily in use are for the most part physical. By means of the pycnometer, vaporimeter, and ebullioscope, we are able to determine with reasonable accuracy the amount of alcohol present in alcoholic beverages and solutions, which seldom contain under one per cent of ethyl alcohol. When, however, the exact estimation of smaller quantities is desired, these methods are unsatisfactory.

The numerous chemical methods for the determination of alcohol depend for the most part on the oxidising action of potassium bichromate, chromic acid, or potassium permanganate. Only a small portion of the research on the oxidising action of these compounds has been done with reference to their oxidation of alcohol. This is partly explained by the previous existence of the physical methods of analysis above referred to and by the fact that while many organic compounds are completely and readily oxidised to carbon dioxide and water, alcohol is oxidised with great difficulty, the oxidation ceasing usually with the formation of acetic acid. The iodoform reaction and the blue colouration produced with a sulphuric acid solution of molybdic acid, furnish tests of the greatest delicacy, and for the most part investigators have been satisfied with a qualitative demonstration of the presence of alcohol when occurring in such small quantities as to preclude the use of the ordinary quantitative methods.

Bodländer (*Pflüger's Archiv*, xxxii., 398), pursuing an investigation similar to that for which the methods here reported were devised, *i.e.*, the estimation of the small quantities of alcohol eliminated in the urine and breath of man, used a standard solution of chromic acid in concentrated sulphuric acid, and estimated the alcohol by determing the amount necessary to completely reduce a given volume of this solution. He states that the oxidation of alcohol is complete; *i.e.*, the products are carbon dioxide and water. Bourcart (*Chem. Centrbl.*, 1890, i., 547), Heidenhain (*Ztchr. Anal. Chem.*, 1893, xxxii., 360), Freyer (*Chem. Ztg.*, xix., 1184; *Ztschr. Anal. Chem.*, xxxvi., 328), and Kuriloff (*Ber. d. Chem. Ges.*, xxx., 741), find, on the other hand, that the oxidation with chromic acid or potassium bichromate ceases with the formation of acetic acid. Rose (*Chem. Centrbl.*, 1888, 308), used potassium permanganate as the oxidising agent, and states that the alcohol was completely oxidised to carbon dioxide and water by decinormal potassium permanganate in a solution that contained 40 per cent of sulphuric acid.

Bodländer's method was tried and found not to give entirely satisfactory results owing to the formation and escape of aldehyd, the amount formed varying with slight changes in the manipulation. On the addition of a dilute solution of alcohol to the concentrated sulphuric acid solution of chromic acid, the odour of aldehyd can be easily detected. Furthermore the end-point is rather difficult to determine.

Potassium permanganate, in the presence of strong sulphuric acid, was tried as an oxidising agent. It was

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* From the *Journal of the American Chemical Society*, xx., No 4.

necessary to heat the solution in order to complete the oxidation, and under these conditions the potassium permanganate is decomposed in the absence of reducing agents. It is believed, however, where only approximate results are required, that the conditions can be determined under which the oxidation is complete, while the decomposition of the potassium permanganate, other than that produced by the alcohol, is very slight. The method used was to mix a definite volume of decinormal permanganate with 40 per cent of its volume of concentrated sulphuric acid, in a glass-stoppered flask. To this mixture the solution of alcohol was added from a burette, in small quantities at a time, and thoroughly mixed with it by shaking. The excess of permanganate was then determined by titration against a standard solution of ferrous ammonium sulphate. For certain purposes in the investigation it was necessary to determine the alcohol vapour contained in a current of air, and since it was found that the permanganate solution was reduced by simply passing the air of the room through it, this reagent could not be used.

As we were not successful in securing the accuracy desired with any of the methods tried, it became necessary to devise one which would give fairly close results for solutions containing as low as 0·01 per cent of ethyl alcohol.

The method adopted depends on the oxidation of the alcohol by an excess of chromic acid in a concentrated sulphuric acid solution, and the determination of the excess of chromic acid by titration against ferrous ammonium sulphate solution, the end-point being established by a few drops of standard permanganate solution. The reagents required for the determination are—

1. A solution of chromic acid in concentrated sulphuric acid.
2. A solution of ferrous ammonium sulphate.
3. An approximately decinormal solution of potassium permanganate.
4. A standard solution of alcohol in concentrated sulphuric acid.
5. Chemically pure, concentrated sulphuric acid.

The chromic acid solution is made by dissolving 2·2064 grms. of chemically pure potassium bichromate in just enough distilled water to effect complete solution, and then making up to 500 c.c. with concentrated sulphuric acid, care being taken not to let the temperature rise to over 100° C. This corresponds to a solution containing three grms. of chromic anhydride in one litre. The reagent preserved in a glass-stoppered bottle is fairly stable.

For the ferrous ammonium sulphate (Mohr's salt) solution 40 grms. of the pure salt are dissolved in water, and, after the addition of 30 c.c. of concentrated sulphuric acid, the solution made up to a litre. Made in this way the solution is very stable, showing but slight changes on comparatively long standing.

The potassium permanganate solution is made by dissolving three and three-tenths grms. of the crystallised salt in a litre of water.

The standard alcohol solution is practically a solution of ethyl sulphuric acid in concentrated sulphuric acid. About two grms. of 5 per cent alcohol (see below) are weighed into a 50 c.c. graduated flask and concentrated sulphuric acid added slowly, keeping the mixture cool to prevent any volatilisation of alcohol by immersion in cold water. After 5 c.c. of the acid have been added in this way the flask is filled to the 50 c.c. mark and the solution mixed by pouring back and forth into a beaker.

The alcohol used in preparing the standard was one of the better grades of commercial alcohol. Its strength was determined with the admirable pycnometer described by Dr. Squibb (*Journ. Amer. Chem. Soc.*, xix., 3). This pycnometer readily gives the specific gravity of alcohol to the fifth or sixth decimal place. Ostwald's pycnometer ("Hand-und Hilfsbuch zur Ausführung physiko-chemischer Messungen," W. Ostwald, p. 110), which has the advantage of being much cheaper, was also found to give quite satisfactory results.

An accurate table for determining the per cent of alcohol in solutions containing 40 per cent of absolute alcohol or over, from the specific gravity, is given by Dr. Squibb in his "Ephemeris" (*Ephemeris*, ii., 541). For solutions containing less than 40 per cent the table ("Bulletin No. 46, Division of Chemistry, U.S. Department of Agriculture," p. 65) used by the Association of Official Agricultural Chemists, is to be recommended.

A practical difficulty arises in weighing out small quantities of strong alcohol owing to its volatility. It is therefore recommended that an approximately 5 per cent solution be first made, from which small quantities can be correctly weighed without material loss. For preparing this solution the following method was found to be the most satisfactory:—A glass-stoppered Schuster dropping bottle, such as is ordinarily used to contain indicators, was weighed when dry and clean. After adding about the required quantity of alcohol its weight was again taken. The alcohol was poured into a previously tared flask, the last traces being removed by careful washing with distilled water. The solution was then made up to the desired weight, and the per cent of absolute alcohol in it calculated.

It is of the utmost importance that the concentrated sulphuric acid used in these experiments be free from organic or other reducing matter.

To find the value of each solution in terms of the other, the ferrous ammonium sulphate is first titrated against the potassium permanganate. A measured volume of the chromic acid solution, generally 10 or 20 c.c., is then poured into 100—200 c.c. of water, enough of the ferrous ammonium sulphate solution added to completely reduce it, and the excess of ferrous ammonium sulphate determined with the potassium permanganate. Twenty c.c. of a chromic acid solution of the above strength oxidises about 17 c.c. of the ferrous ammonium sulphate solution. Owing to the viscosity of the chromic acid solution it is necessary to adopt a definite method of delivery in order to obtain the same quantity each time. This result was secured by allowing the solution to run freely from an ordinary pipette made to deliver 10 c.c. Toward the end of the delivery the drops ceased quite suddenly to fall in quick succession, and followed each other only at intervals of several seconds. The first "slow" drop was taken and the pipette removed immediately. This method apparently gave equal volumes of liquid.

The amount of chromic acid required to oxidise a given weight of alcohol was determined by means of the standard solution of alcohol in concentrated sulphuric acid. Ten c.c. of chromic acid solution were drawn off into a small flask, and a measured amount (about 3 c.c.) of the standard solution of alcohol added from a burette.[*] The mixture was heated with constant agitation over a free flame to 98° C.[†] (a thermometer being held in the solution) and kept at about this temperature for five minutes. Under these conditions no aldehyd was formed. After cooling the solution it was poured into 200 c.c. of water, ferrous ammonium sulphate added from a burette until the red colour of the chromic acid had entirely disappeared, and the excess of ferrous ammonium sulphate titrated back with the potassium permanganate.

The standard solution of alcohol used contained 237·6 m.grms. of alcohol in 100 c.c. In four titrations of this solution we obtained the following results. (See Table, next column).

Since a cubic centimetre of the alcohol solution contained 2·376 m.grms. of alcohol, 1 c.c. of the ferrous am-

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[*] Considerable time is required for the sulphuric acid solution to run down the sides of the burette. The readings should not, therefore, be made until it is ascertained that the meniscus is stationary.

[†] According to Cross and Bevan (*Journ. Chem Soc.*, liii., 889), chromic acid in concentrated sulphuric acid solution gives off oxygen at 105° C. Numerous tests showed no decomposition of the chromic acid solution after five minutes' heating at 98° C.

	Alcohol solution. C.c.	Equivalent in ferrous ammonium sulphate solution. C.c.	Ferrous ammonium sulphate solution equivalent to 1 c.c. of alcohol solution. C.c.
I.	4·00	9·70	2·43
II.	4·95	12·00	2·42
III.	2·95	7·20	2·44
IV.	3·10	7·60	2·45
		Average..	2·43

monium sulphate solution would be equivalent to 0·978 m.grms. of alcohol. This factor was used in calculating the alcohol in the other solutions.

In order to test the accuracy of the determination, solutions of different strengths were made by the method used in preparing the standard solution.

The following results were obtained upon analysis:—

	Weight of alcohol.		Volume of solution.	Per cent of alcohol.	
	Calculated. M.grms.	Found. M.grms.	C.c.	Calculated. Per cent.	Found. Per cent.
I.	38·18	38·18	100	0·038	0·038
II.	30·63	30·05	50	0·071	0·070
III.	853·00	885·00	500	0·171	0·177
IV.	7·24	7·12	100	0·00724	0·00712
V.	11·01	11·23	50	0·02202	0·02246

An extremely dilute solution was made by diluting 12·34 m.grms. of alcohol to 250 c.c. The solution therefore contained 0·00494 per cent of alcohol. The result obtained by titration was 0·00508 per cent, an error of about one ten-thousandth of 1 per cent of alcohol.

In order to compare the accuracy of the method with that of Squibb's pycnometer for dilute solutions of alcohol, 31·44 grms. of 90·61 per cent alcohol was made up to 994·5 grms. with water, giving a 2·865 per cent solution. With Squibb's pycnometer the result was 2·95 per cent when calculated from a table in the "Ephemeris" (ii., 563), and 2·84 per cent when calculated from a more recent table (*Bulletin No.* 46, p. 65, Division of Chemistry, U.S. Department of Agriculture). By titration with the chromic acid the strength was determined to be $2\frac{8}{10}$ per cent.

As previously stated, one of the conditions to which the method must apply, was the determination of small quantities of alcohol in an air current.

Concentrated sulphuric acid, according to our experiments, removes alcohol from an air current even more completely than it does water. The apparatus with which this great affinity of sulphuric acid for alcohol was determined consisted of a system arranged as follows:—A current of air drawn by means of an ordinary Chapman filter-pump passed successively through a U-tube filled with cotton, a gas-washing cylinder containing concentrated sulphuric acid, a U-tube filled with soda-lime, a U-tube containing a known amount of alcohol, a cylinder similar to the first containing concentrated sulphuric acid, a 12-inch piece of combustion tubing containing a layer of copper oxide kept at a red heat by a four-tube burner, and a U-tube containing glass beads covered with about 10 c.c. of barium hydroxide solution, which in turn was connected by a rubber tube to the filter-pump. The tube with cotton was used to remove dust from the air. The sulphuric acid in the first cylinder removed the water, and the soda-lime the carbon dioxide. The air then passed over the alcohol and carried some of it into the sulphuric acid in the second cylinder. In case any of the alcohol was not absorbed by the sulphuric acid it would be burned by the hot copper oxide to form carbon dioxide, which would produce a precipitate in the barium hydroxide solution. Air was passed through the apparatus at the rate of 600 c.c. a minute.

(That it is possible to remove the alcohol quite completely from a current of air passing at a much more rapid rate than this, was subsequently demonstrated with a slightly modified apparatus. Owing to the fact that a rapid air current caused the combustion of the rubber stopper in the end of the short tube containing the copper oxide, by the hot air drawn against it, a tube 30 inches long was used and heated only at one end. The barium hydroxide U-tube in the apparatus above described also was not very satisfactory for rapid currents of air, and was therefore replaced by a gas-washing cylinder containing about 20 c.c. of barium hydroxide solution. A current of air containing alcohol vapour drawn through this apparatus at the rate of 2100 c.c. a minute, produced only a slight turbidity in the barium hydroxide solution in the course of fifteen minutes. When the cylinder containing sulphuric acid was removed from the system, however, a heavy precipitate was instantly formed).

(To be continued).

ON THE
PERIODIC SYSTEM AND THE PROPERTIES OF INORGANIC COMPOUNDS.*
PART I.

By JAMES LOCKE.

THE problems set before the inorganic chemist by the periodic system, which have directly or indirectly guided almost all the inorganic investigations of the past thirty years, may be divided, roughly in the abstract but very sharply in the results obtained, into two classes. The one, of the fruitfulness of which no one can complain, deals with the superficial group-relations which exist between the members of the various families. Their solution leads to what may be called the development of group analogies. The problems of the second class, on the other hand, have either been entirely neglected, or their study has yielded only the most unsatisfactory results. These have had to do with the contractions of fact which the system, as formulated by Mendeleeff, involved, and to which the system should in course of time adapt itself. But all the more important inconsistencies which it presented in the year 1870 still remain, and are finally recognised as facts which, for the sake of a convenient principle, must not be forced into a conspicuous position. The behaviour of the elements of low atomic weight; the appearance of one and the same element in more than one degree of oxidation; the properties of the platinum metal; either receive no expression in the system, or they stand in direct contradiction to its laws. The difficulties involved, however, are confined chiefly to the compounds. The relations between the elements, *as elements*, are in almost every case clearly pointed out in the usual tables. This is true in regard to both the physical and chemical properties of the elements themselves. In this paper, therefore, only that part of Mendeleeff's law will be discussed which says that the *nature of the compounds of an element is also a function of its atomic weight.*

Of the 65 elements having places in the system, 9 of them, iron, cobalt, nickel, and the platinum metals, are put in a vertical row by themselves where they form the so-called 8th family, a family which may be said to fall outside the system proper. In this group many of the regularities which can be traced through other families are wanting.

The valency of the elements increases by one in each successive vertical row of the system, until the fourth is reached, after which each family yields two series of compounds, the one of increased, the other of decreased valency. In the potassium-nickel series, for instance, the various elements should enter into compounds with the valencies:

$$\mathrm{K}^{\mathrm{I.}},\ \mathrm{Ca}^{\mathrm{II.}},\ \mathrm{Sc}^{\mathrm{III.}},\ \mathrm{Ti}^{\mathrm{IV.}},\ \mathrm{V}^{\mathrm{V.}},\ \mathrm{Cr}^{\mathrm{VI.}},\ \mathrm{Mn}^{\mathrm{VII.}},\ (\mathrm{Fe},\ \mathrm{Co},\ \mathrm{Ni})^{\mathrm{VIII.}}$$
$$\mathrm{V}^{\mathrm{III.}},\ \mathrm{Cr}^{\mathrm{II.}},\ \mathrm{Mn}^{\mathrm{I.}}.$$

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* From the *American Chemical Journal*, xx., No. 7.

So, since chromium falls within the 6th family, the greatest weight is laid upon the fact that chromic acid and its salts show such close analogy to sulphuric acid and the sulphates. The fact that potassium permanganate is isomorphous with the perchlorate, and like the latter only sparingly soluble in cold water, likewise assumes the utmost importance. If compounds of iron, cobalt, and nickel were known, in which these elements were octavalent, they, too, would possess the greatest theoretical value. But, with the exception of nickel carbonyl, a doubtful case of octavalency, these theoretically necessary compounds have never been obtained. Up to the present no one has succeeded in getting beyond the ferric acid of hexavalent iron.

That the decrease in valency, on the other hand, must stop before the 8th family is reached is obvious, for the 7th family is itself univalent, and a further decrease would prevent iron, cobalt, and nickel from forming any compounds at all. But this regularity ceases still further on—with chromium. No univalent manganese compounds have been obtained. Now, inasmuch as the iron, cobalt, and nickel compounds fail to conform with a regularity which can otherwise be traced throughout the entire system, they are assigned an entirely different rôle from that of other elements. They form transition stages, so to speak, from the manganous salts to the copper compounds of the next horizontal row. But this transition is not from the compounds of univalent manganese to those of univalent copper. Univalent manganese is unknown. It is from divalent manganese to divalent copper—to copper in a degree of oxidation which in no way corresponds to the position of this element in the system, and the salts of which have nothing more in common with the cuprous compounds, than has sulphuric acid with hydrogen sulphide; the same element can be obtained from both, and even then the road is by no means a smooth one, for directly before manganese stands chromium, and since divalent manganese has no place in the system, the chromous salts must be regarded as the true starting-point for the transition. But the transition from the unstable divalent and stable trivalent derivatives of chromium to those of ferrous and ferric iron is through a manganese in which the relative stability in the two degrees of oxidation is exactly the reverse.

I know I lay myself open here to the charge of expecting too much from the system. But why? Here is a great law of nature, the correctness of which no one can doubt. But in order to illustrate this law, an empirical arrangement of the elements is formed, and this arrangement we are all too apt to confuse with the law itself. The periodic system is satisfactory enough for the elements. Lothar Meyer's curves of the atomic volumes and melting-points prove this. For the compounds it is *unsatisfactory*. And in order to find out how the law does apply to compounds, we must sift out and discuss the discrepancies which the system shows in regard to them.

As with iron, cobalt, and nickel, so it is with all the other members of the 8th group. These metals, at the time of the promulgation of the periodic system, were assigned a position which, satisfactory though it was in illustration of their properties as elements, was in regard to their compounds absolutely abnormal; and no amount of investigation and speculation, with the periodic system as a basis, can clear up the contradictions which their position entails.

A second point upon which no light has been thrown lies in the behaviour of the so-called "typical elements." These, as Ostwald remarks, instead of being types of the families at the head of which they stand, have in the majority of cases properties directly at variance with those of the other members of their respective groups. In his "Principles of Chemistry" Mendeleeff says:—"The elements of the first two series have the least atomic weights, and in consequence of this very circumstance, although they bear the general properties of a group, still they show many peculiar and independent properties. These lightest elements are:—

H;
Li, Be, B, C, N, O, F;
Na, Mg, .., .., ...

As Mendeleeff left these elements, "typical," so they have remained, and the history of thirty years contains no mention of a successful attempt to unite them more closely than by that ill-fitting word to the groups to which they should show analogies.

Lithium is the lightest of all the elements having places in the system. It should, therefore, from the above, have the greatest number of independent properties of any of the typical elements. Or, one should at least expect to find metallic lithium and lithium compounds varying from the higher alkali metals and their derivatives in one and the same degree, since their departure from the rest of the group is conditioned by one and the same cause. The abnormal behaviour of the other typical elements should be along the same lines as in the case of lithium and its compounds. The essential properties of metallic lithium stand in strictest analogy to those of the other alkali metals. Metallic beryllium fits in accurately in the series formed by magnesium, zinc, cadmium, and mercury. Between boron and aluminium the analogy is less clear; but it appears again in full force in the properties of free carbon and silicon. The two elements show in their physical properties, allotropic modifications, and indifference to reagents, the strongest similarity. Fluorine and chlorine, in the elementary state, present the most striking analogies; and the gradations in character which the free halogens undergo with increasing atomic weight, from fluorine through to iodine, yield one of the most perfect chemical series imaginable.

Of the seven elements making up the first horizontal row, therefore, at least four possess, *in the elementary state*, properties closely akin to those of the subsequent elements in their respective families, and complete the series which the latter form.

Now, if the periodic system is true for compounds as well as for the elements themselves, then the compounds of analogous elements must be analogous—a simple deduction from the law which is not altered in its bearing, by the fact that the elements with which we happen to be dealing fall within the so-called typical class. If the low atomic weights, therefore, of the four elements, lithium, beryllium, carbon, and fluorine, are not of such influence as to prevent their ranking as they should, in their respective families, we must expect that their compounds will also show analogy to those of the other members of their groups. The compounds of lithium vary more or less from those of the other alkali metals, it is true; its phosphate and carbonate especially are less soluble; but, nevertheless, the lithium salts in general possess the characteristics of alkali derivatives, to an extent which would certainly prevent anyone from considering lithium as anything but an alkali metal. Carbon and silicon likewise bear close relationship in their compounds. The property of carbon which gives rise to organic radicals and existence of such a multitude of combinations between but a few elements, the ability of the carbon atoms to unite with one another, likewise appears in silicon. The silicon hydrides, the various chlorides, bromides and iodides, silicon-chloroform, and the complex oxygen compounds, such as silico-oxalic and mes-oxalic acids, illustrate fully the strong similarity between the influence of tetravalent carbon and that of silicon upon their compounds.

The law, and its expression by the periodic system, therefore, holds good in the case of lithium and carbon, and no fault can be found with the typical behaviour of the two elements. Now, if the effect of small atomic weight upon both lithium and carbon is too slight to cause in the nature of their compounds any great variation from that of their homologues, one has a perfect right to assume that this separating influence will not be greater in an element which, in its atomic weight, lies between the two; but after a comparison, unprejudiced by the fact that an analogy between the compounds of beryllium and magnesium is required by their positions in the system, can a single trace of true resemblance be found between them, or between beryllium derivatives and those of any other element in the second vertical row? Magnesium hydroxide and beryllium hydroxide are both dibasic, it is true. But there the similarity ceases.

A strongly distinctive feature of all magnesium, zinc, and cadmium salts is seen in their behaviour toward ammonia and ammonium salts. They also have a pronounced tendency to form double salts with the compounds of other metals. Their oxides are insoluble in water, but soluble even in weak acids. Calcium, strontium, and barium, on the other hand, are characterised by their soluble, strongly alkaline hydroxides, by their difficultly soluble sulphates, and by the difficulty with which they enter into double salts. These are group characteristics, the presence of any one of which indicates the others. They give a tone to, and define the nature of, all the compounds of the two series. But to beryllium salts not one of them applies. Similar to magnesium though the metal be, its compounds show perfect indifference to ammonium salts; they form no double salts,* and the oxide is practically insoluble even in strong, hot acids; as little soluble, in fact, as alumina. This last fact, together with the ready solubility of the sulphate and of the fluoride, and the insolubility of the sulphide, &c., prevent any comparison of the beryllium compounds with those of the alkaline earths.

With fluorine, the nature of the compounds of which it will be unnecessary to discuss in full, the case is similar, although its atomic weight is nearly three times as great as that of lithium. The properties of the free element show it to be a pronounced halogen, with characteristics which one would expect to find in a halogen of lower atomic weight than chlorine. But its compounds are not only widely different from those of chlorine, but they often vary in a direction contrary to that of the gradations observed in the rest of the series. Fluorine, it is true, forms in common with the other halogens an acid of the type HR. But in distinction from hydrochloric, hydrobromic, and hydriodic acid, hydrofluoric acid has a remarkably low molecular conductivity; and its salts, in the majority of cases, have properties which are directly the opposite of those of the chlorides, bromides, and iodides. The most pronounced chemical characteristic of the halogen acids certainly lies in the solubility of their salts with heavy metals, and the insolubility of the silver, cuprous, and mercurous compounds. The *fluorides* of silver and mercury, on the other hand, are readily soluble: those of calcium, strontium, barium, magnesium, manganese, iron, cobalt, nickel, chromium, cadmium, copper, bismuth, lead, and others are either sparingly soluble or dissolve only in an excess of hydrofluoric acid. In the readiness with which fluorine enters into metallofluoric acids is seen another great distinction from the other halogens. In this, as in many of its other properties, it approaches very closely to cyanogen. Hydrofluoric and hydrocyanic acids and their salts have, in fact, little more in common with hydrochloric, hydrobromic, hydriodic acids, and the halogenides, than the fact that they are monobasic or derivatives of monobasic acids.

We have, therefore, in lithium, beryllium, carbon, and fluorine, four typical elements which in the free state, *as elements*, stand in close relationship to the other elements of their respective groups. In two of them, lithium and carbon, the influence of their low atomic weights is not such as to deprive their compounds of the chemical nature which characterises the derivatives of their analogues. The others, although one of them lies *between* lithium and carbon, and the other has an atomic weight almost large enough to take it out of the typical class, fail to show analogy to their homologues; that is, to satisfy the requirements of the system, as soon as they pass from the free state into combination.

These are contradictions which even the mysterious influence of a low atomic weight will not explain. They were known in 1870, and they stand to-day. With the development of organic chemistry, and the increase in the number of bodies known, which could not be explained by the laws of valency alone, stereochemistry appeared. Molecular compounds have been the subject of numerous theories, of which one at least, that of Werner, promises to bear fruit; but the inconsistencies shown, in reference to the other elements, by those of low atomic weight, the exceptions to a law more far reaching than that of valency itself, have remained untouched, simply in recognition of the fact that it was hopeless to look for any explanation for them which could be reconciled to the system. And why? Because the inorganic chemist, in standing upon the periodic system, has been unable to dissociate in his mind the chemical compound from the elements of which its formula contains the symbols.

Of the work done in the development of group analogies little need be said. This has been the only successful field of investigation which the formulation of the system opened. But it may be well to point out briefly certain inconsistencies which are involved in the development of these analogies between neighbouring metals in the horizontal rows.

(To be continued).

CORRESPONDENCE.

METARGON.

To the Editor of the Chemical News.

Sir,—Metargon is said to be an elementary substance having the primary characteristic of being a gas obtained by the volatilisation of a "white solid" (amounting to about one per cent), which separates during the liquefaction of argon, as stated by Prof. Ramsay and Mr. Travers in their Royal Society papers on the "Companions of Argon:"—"The argon separated as a liquid, but at the same time a considerable quantity of solid was observed to separate partially round the sides of the tube, and partially below the surface of the liquid." Further, "inasmuch as the gas differs very markedly from argon in its spectrum and in its behaviour at low temperatures, it must be regarded as a distinct elementary substance, and we therefore propose for it the name 'Metargon.' It would appear to hold the position towards argon that nickel does to cobalt, having approximately the same atomic weight for different proportions."

Now a year ago Lord Rayleigh was kind enough to allow me the use of a sample of pure argon for the purposes of liquefaction. The gas, amounting to 250 c.c., was enclosed in a sealed bulb, to which was attached a narrow quill tube for easy condensation in liquid air. I have repeatedly liquefied this sample, and have always obtained a perfectly clear fluid argon free from turbidity or opalescence. In previous papers I have shown that very small fractions of a per cent of impurity of a gaseous substance separating as a solid, the chief constituent being a liquid, under the experimental conditions, can be detected in this way. Thus the 0·04 per cent of carbonic acid in dry air gives an opalescent liquid air when similarly treated, and the same thing occurs with oxygen containing less than 0·1 per cent of chlorine. It would indeed be strange if anything like 1 per cent of a gas giving a white " solid at the

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* Certain double fluorides must be noted as exceptions to this statement. The double sulphates, phosphates, &c., known, may be disregarded, as they can be represented by simple constitutional formulæ, and this formation is of less significance than that of double halogenides, and the like. Both calcium and strontium yield double sulphates.

temperature of liquid air" could, under similar circumstances, escape detection, if present, in the Lord Rayleigh sample of argon. The question is, what has become of the metargon of Prof. Ramsay and Mr. Travers?—I am, &c.,

James Dewar.

Royal Institution,
August 2, 1898.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvi., No. 21, May 23, 1898.

Further Researches on the Reactions Developed between Pyrogallol and Oxygen in the presence of Alkalis.—M. Berthelot.—The author finds that the oxidation varies considerably, according to the alkali present, either potash, soda, baryta, or ammonia. The observations and estimations made show that purpurogallol is generally formed. At the same time there is evidence that the pyrogallic molecule is destroyed by an oxidation which breaks up the fundamental cyclic system. This destruction may be imagined to take place in the following manner:—Of the three molecules of acetylene, which by their junction have helped to form a molecule of benzene—that is to say, a relatively saturated polymer—two are broken up and changed into carbonic acid and water, while the residue of the third remains united with three other molecules of the original pyrogallol in such a manner as to constitute a new and more complicated cyclic system of the triphenylethane order.

Phosphorescent Mixtures formed by Sulphide of Strontium.—J. R. Mourelo.—Various experiments are described with mixtures of sulphide of barium with sulphide of strontium, sulphide of strontium with sulphide of calcium, and sulphide of calcium with sulphide of barium. The results obtained have enabled the author to establish certain practical laws, which are of some interest:—To produce phosphorescence there must be at least 2½ per cent of either of the active bodies present; after this, the degree of phosphorescence increases with the proportion of the active body. In every case the exposure to light should be longer in the case of a mixture. Chloride of sodium or sub-nitrate of bismuth, added before heating, will always increase the phosphorescent power. As for the colour of the phosphorescence, that varies with the proportion of the different active bodies present in the mixture, but as a rule it is green that predominates.

Limits of Inflammability of Combustible Gases.—H. Le Chatelier and O. Boudouard.—(See p. 62).

The Spectral Analysis of some Non-conducting Minerals by their Melted Salts, and Reactions of the Elements.—A. de Gramont.—This article has already been inserted in full.

Synthesis of Safranine.—G. F. Joubert.—This paper is to a great extent the continuation of a discussion with M. Nietzki as to the correctness of the *asymmetric* formula of safranine; but it is shown that an estimation of the nitrogen and the chlorine gives the following results:—

	N per cent.	Cl per cent.
Calculated for $C_{20}H_{16}N_7O_6Cl$ ..	20·18	7·31
Found	19·84	8·02

Action of Chloride of Aluminium and of Chlorine in the presence of Chloride of Aluminium on Anhydrous Chloral.—A. Mouneyrat.—500 c.c. of anhydrous chloral were poured into a flask of 1000 c.c. capacity, fitted with a vertical condenser; then 250 grms. of perfectly anhydrous and finely ground chloride of aluminium were added a little at a time. The mass, then quite solid, was heated up to 75—80°, then, when the material was quite fluid, a current of dry chlorine was injected. This gas is entirely absorbed, and an abundant disengagement of hydrochloric acid gas ensues. After the lapse of some time, the interior surface of the flask, as well as the tube leading in the chlorine, become coated with magnificent white crystals having a very pronounced smell of camphor. When the chlorine is no longer absorbed, the then solid mass is put into dilute hydrochloric acid—a little at a time. Torrents of hydrochloric acid gas are then given off, as well as a small quantity of $COCl_2$, while a white powder, smelling slightly of camphor, rises to the surface. This body, which is purified by sublimation, melts at 187—188° in a capillary tube. Analysis gives it the formula C_3Cl_6.

Estimation of Phosphoric Acid in Superphosphates.—Leo Vignon.—The author points out that the method of estimation by difference is more to be trusted than that by the direct method. It is easy, he says, to understand why the ammonio-magnesic phosphate, by reason of its mass, has a greater tendency to deposit integrally in a mixture of water and citrate than in citrate alone, which might be poor in phosphoric acid.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxx., January 10, 1898.

Remarks on the Memoir by M. Hermann on the subject of the Number of the Isomeric Paraffin Carbides.—S. M. Losanitsch.—The author discusses the convenience of M. Hermann's method for calculating the number of isomeric saturated fatty carbides in C*n*.

New total Synthesis of Glycerin and Dioxyacetone.—O. Piloty.—Dioxyacetone is easily obtained by adding 15 grms. of bromine to a solution of 10 grms. of its oxime in 100 c.c. of water. N_2O is given off, and the temperature rises to 40°. It is then neutralised with $PbCO_3$ and Ag_2O, and the filtrate evaporated at 30° *in vacuo*, taken up with absolute alcohol, and precipitated with ether. The syrupy precipitate is treated in the same manner, and at length a viscous product is obtained which solidifies over H_2SO_4; it is dioxyacetone. The return is 95 per cent of theory. It crystallises from boiling water in prismatic plates, fuses at 70—75°, is soluble in H_2O and organic solvents, except ether and ligroin. Dioxyacetone, $CH_2OH.CO.CH_2OH$, easily forms polymers, of which one is crystalline and melts at 155°, while the other is amorphous. The bisulphite compound, $C_3H_7O_5SNa$, crystallises in dilute alcohol in white needles.

Preparation of the Acetals.—E. Fischer and G. Giebe.—Many aldehyds can be transformed into the corresponding acetals by treating them with a dilute alcoholic solution of hydrochloric acid gas. Ordinary acetal was prepared by mixing 20 grms. of aldehyd with 80 grms. of alcohol containing 1 per cent of hydrochloric acid gas. It was left for eighteen hours in the cold; 100 c.c. of water containing sufficient K_2CO_3 to neutralise the HCl was added, and the product extracted with ether. The return was 60 per cent; with œnanthol, the return was 70 per cent. It boils at 205°. Dimethylformal can be obtained by treating formic aldehyd by 1·5 times its volume of alcohol containing 2 per cent of HCl, and 1·5 parts of $CaCl_2$. It is heated for fifteen hours and distilled. The acetal from glycolic aldehyd is prepared in a similar manner. The preparation of several other acetals is described. The process does not appear to be easily applied to the oxyaldehyds.

Tetramethyluric Acid.—E. Fischer.—This acid is prepared by the direct methylation of uric acid; it melts at 228° and has a bitter taste. One part of the acid dissolves in three parts of boiling water, twenty-seven parts of boiling alcohol, or thirty-nine parts of cold water. When heated with 1 per cent $POCl_3$ at 160°, it is transformed into chlorocafein. A 1 per cent solution of tetramethyluric acid, saturated with Cl, gives allocafein fusible at 206°. It is slightly soluble in water, and easily so in sulphuric acid and the alkalis. Boiling baryta-water decomposes it, giving mesoxalic acid. The oxidation of tetramethyluric acid is shown by the equation $C_9H_{12}N_4O_3+O+H_2O=C_8H_9N_3O_5+CH_3.NH_2$.

The Optical Properties of Tannin.—P. Walden.—Tannin is strongly dextrogyre, but the formula generally ascribed to it does not contain any asymmetric carbon. If we admit that tannin is not a definite chemical compound, but a mixture, then this anomaly disappears. In fact, the author has succeeded in separating several portions having entirely different rotatory powers, and he is of the opinion that tannin owes its activity to a foreign matter which is always present in variable, though small, quantities.

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THE CHEMICAL NEWS.

Vol. LXXVIII., No. 2020.

LABORATORY NOTES.

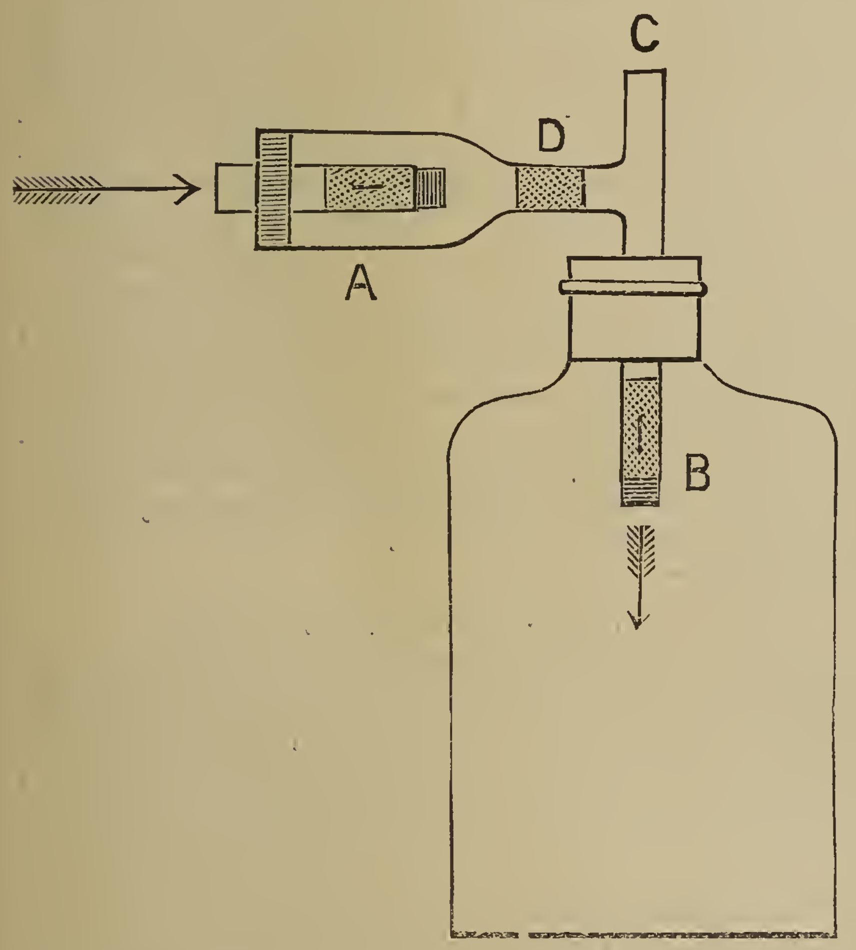
By HORACE JERVIS.

A Simple Pump.

The accompanying figure represents an apparatus which has been used at itinerant lectures to provide a stream of water, or air, or to serve as an air-pump.

It is necessary to perforate the rubber stopper so as to receive an additional tube, which should reach nearly to the bottom of the bottle. The piece of stout soft rubber tubing, B, is made into a Bunsen valve with a sharp razor. A similar valve is fitted into a glass tube, as at A. The other necessary part of the outfit is a cycle tyre inflater, which is attached to C, the open end of the T-tube.

On forcing down the piston of the inflater the air passes through the slit B into the bottle, and is prevented from passing through A, because the compressed air can act only on the outer circumference of the rubber tubing, and so more and more tightly closes the slit. On raising the piston the air is drawn through A, but, for the reason just stated, cannot pass through B again into the inflater.



The alternate motion of the piston then speedily accumulates air, under pressure, in the bottle, and it thus supplies—through the additional tube not shown—a stream of air, or, if water has been placed in the bottle, a stream of water. The arrangement admirably serves to illustrate the transmission of vibrations along a water column (Chichester Bell's experiment), or other phenomena of surface tension which may be illustrated by a thin stream of liquid.

If A (from the joint D) and B are changed about, then an upward action of the piston partially exhausts the bottle, and the downward motion drives the air through the valve B. If then the bottom of the bottle be cut off, the edges smoothed and fitted to a piece of ground glass, we have an efficient lecture-room air-pump.

It is hardly necessary to explain that a common form of tyre inflater is merely a rubber-tipped rod working in a brass tube, and so could be easily made. But they can be borrowed anywhere now-a-days.

ON THE
ESTIMATION OF ARSENIC IN ANTIMONY AND IN OTHER METALS.

By O. DUCRU.

I. Metallic commercial antimony described as "purified" contains, as a rule, small quantities of iron, lead, copper, and sulphur, besides variable proportions of arsenic: the estimation of this latter body, which is particularly important with regard to certain of its applications, presents, as is well known, serious difficulties.

The method usually followed consists in dissolving the metal in an aqua regia containing an excess of hydrochloric acid, and in separating the sulphides insoluble in the alkaline sulphides: the sulphides of antimony and arsenic are in their turn oxidised, and the arsenic is precipitated in the form of ammonio-magnesic arseniate. Rivot, who described this method in some detail, previously isolated the sulphide of arsenic by treating with moderately dilute hydrochloric acid; he gives it as his opinion that this is sufficient for the estimation of the arsenic.

Independently of causes of error inherent in the use of the arseniate (solubility, carrying down of salts, &c.), this method leads to another which may be of importance:—On account of the volatility of chloride of arsenic, it is difficult to avoid losses, either during the solution of the metal or during the attack of the sulphides. It is easy to convince oneself of this, by carrying the vapours into an appropriate apparatus. There is also another thing: the proportions of arsenic found by different analysts, in the same sample of antimony, generally show considerable differences, and these are always below the truth.

II. This estimation can be made in a very simple and precise manner, by applying to an antimony a method described as the *distillation* or *ferric chloride* method, which is employed in the laboratories of certain works for the estimation of arsenic in metallic copper. (This method is due to Dr. John Clark, *Chem. Industry*, May 1887, p. 352). *The method of working is as follows:*—The sample for assay, about 5 grms., coarsely powdered, is placed in a tubulated retort, or a flask for fractional distillation, with 100 c.c. of ferric chloride prepared as follows, and 200 c.c. of pure hydrochloric acid of the ordinary strength (D=1·17). The retort is united to a condenser* terminated by a tube plunging into a graduated flask containing 50 c.c. of water.

We then distil; the antimony is rapidly dissolved, and, each time that 100 c.c. have passed over, we add 100 c.c. of hydrochloric acid by means of a funnel placed in the top of the retort.

When 300 c.c. have been collected in this manner, all the arsenic will generally be found in the distillate; this is the case for proportions of arsenic reaching up to 10 per cent, a higher figure than is met with in practice.†

It is well known that under these conditions the distillate contains a little antimony; this is separated by a second distillation.‡

The receiving vessel is washed with hydrochloric acid,

---

* The use of condensers with large tubes is particularly convenient; the neck of the retort is drawn out and slightly curved.

† That all the arsenic has passed over in the distillate can be verified by passing a current of sulphuretted hydrogen through the hydrochloric solution *diluted with its own volume of water*; if there is no precipitate *after several minutes* all the arsenic has passed over.

‡ I shall eventually show how this second distillation can be avoided.

which is then added to the collected liquid; we thus get a total volume of about 400 c.c., which is distilled until 300 c.c. has passed over. All the arsenic will be found in this portion; this can again be verified by testing the liquid in the retort, diluted with its own volume of water, with a current of sulphuretted hydrogen. To arrest the first traces of hydrochloric acid passing over, it is advisable to put about 100 c.c. of water in the receiver.

This second distillation can be considerably shortened, by previously adding to the solution 50 to 100 c.c. of concentrated sulphuric acid; it will then generally be sufficient to distil 150 c.c.; it can be proved, as above, that all the arsenic has gone over. It is as well, in this case, to facilitate the distillation by keeping a small current of air passing through the boiling liquid.

The hydrochloric solution thus obtained is diluted with water and precipitated with hydrosulphuric acid. The precipitate of sulphide of arsenic is washed in the ordinary manner, and weighed on a filter or in a tared crucible.

III. *Preparation of the Solution of Ferric Chloride.*—We use a solution containing about 150 grms. of iron per litre, obtained by attacking 800 grms. of French nails by a mixture of 2 litres of pure hydrochloric acid and 2 litres of water: when the attack is ended, the liquid is saturated with sulphuretted hydrogen, allowed to stand, and filtered; the sulphuretted hydrogen is driven off by heat, and a current of chlorine is passed through the solution until the iron is completely transformed into the ferric salt; the excess of chlorine is driven off by a current of air in the ordinary manner. Finally, we make the volume up to 5 litres by adding pure hydrochloric acid.

The reagent and the hydrochloric acid are simultaneously assayed by distillation, by placing in the retort 15 grms. of ferrous sulphate free from arsenic.

IV. I have further found that this method, with a few slight alterations, may be applied to a large number of metals, such as irons and steels, lead, tin, zinc, &c., and to alloys, such as bronze, &c. It can be used for the detection and estimation of small proportions of arsenic which are frequently met with, or for the analysis of alloys or combinations in which arsenic is present in notable quantities. I propose to give more complete information on this subject in a future paper.—*Comptes Rendus*, vol. cxxvii., No. 4, July 25, 1898.

ON THE NATURE OF THE DIDYMIUM WHICH ACCOMPANIES THE YTTRIA OBTAINED FROM THE MONAZITE SANDS.

By G. URBAIN.

M. Boudouard recently announced that he had separated from the yttria of the monazite sands a didymium earth but slightly soluble in potassic sulphate, and presenting all the characteristics of neodymium.

I have pointed out in a previous note that the earth derived from the head crystallisations of the yttric ethylsulphates, entangle the didymium which had escaped the preliminary elimination of the earths of the ceric group by sulphate of potash.

I eliminated this didymium by fresh precipitations by sulphate of potash, and I noted that even if the didymium thus obtained had all the characteristics of neodymium, it could not be entirely identified with neodymium, and it also contained a large proportion of foreign earths.

The spectrum of this substance showed besides the bands of neodymium, the bands of M. Soret's X, also some bands of erbium and praseodymium. In all cases these bands were very faint. Some fractionations by sulphate of potassium in the presence of alcohol gave evidence of the presence of earths of the terbic group, and fractionation by ammonia in the presence of H_2O_2 sufficed to prove the presence of cerium. Thus this substance is actually very rich in neodymium, and I entirely agree with M. Boudouard when he recommends this new method as being likely to give better results than that adopted by M. Auer von Welsbach for the preparation of neodymium.

It is interesting to remark that among the bands of praseodymium that have been observed in this substance rich in neodymium, the band $\lambda = 469$ is distinctly visible, while the bands $\lambda = 444$ and $\lambda = 482$ are doubtful. M. Demarçay (*Comptes Rendus*, vol. civ., p. 580), and MM. Krüss and Nilson (*Deut. ch. Ges.*, vol. xx., p. 2134), made analogous observations on the variation of the relative intensities of these bands.—*Bull. Soc. Chim.*, Series 3, vol. xx., No. 9.

ON THE

PERIODIC SYSTEM AND THE PROPERTIES OF INORGANIC COMPOUNDS.*

Part I.

By JAMES LOCKE.

(Concluded from p. 70).

One of the pronounced features of the periodic system is the regularity with which the valency of the elements increases in the successive vertical rows—a regularity to which in fact so much importance is attached, that Mendeleeff can say without fear of criticism, "PbO_2 is the normal salt-forming oxide of lead, as are Bi_2O_5, CeO_2, TeO_3, of bismuth, cerium, and tellurium!" According to Mendeleeff, when an element forms two series of compounds, as copper, for instance, in one of which it has the same valency as its neighbour in the horizontal row, its compounds in this degree of oxidation must be similar to those of its neighbour. This rule is well illustrated in the case of copper, for the cupric compounds do bear a very close resemblance to those of the next element, zinc. But examine the rule in its full extension. The formation of an alum by any trivalent metal is rightly regarded as characterising its behaviour throughout all its compounds in this degree of oxidation, and sharply distinguishes its sesquioxide from those of another great class of elements, the rare-earth metals. Associated with the formation of alums is the behaviour of the cyanides toward potassium cyanide. All the sesquioxides† which form alums yield soluble double potassium cyanides, the great majority of which have the formula $K_3V(CN)_6$.

In the series—

K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni,

the most typical double cyanide is formed by iron; that of cobalt is also stable, and on the other side we find an analogous salt formed by manganese, "owing to its proximity to iron." But chromium, beyond manganese, also forms one; and from some experiments which I myself have made, I find also that potassium vanadicyanide, $K_3V(CN)_6$, is not only capable of existence, but a well-defined compound. We have here the character which the atomic weight 56 lends to the compounds of trivalent iron exerting an influence upon that of one element to the right and three elements to the left. With the alums the case is still more remarkable. These bodies are formed by cobalt, iron, manganese, chromium, vanadium, and titanium; or by six of the ten elements in a row. And not only that; scandium, the metal next to titanium, not only forms a sesquioxide, but this is its only degree of oxidation. Its compounds, however, have the properties characteristic, not of ferric and aluminium salts, but of the rare earths. And, nevertheless, the close proximity of

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* From the *American Chemical Journal*, xx., No. 7.

† The only exception is in the case of aluminium, the cyanide of which is decomposed by water. Potassium cyanide precipitates the hydroxide.

this element to titanium does not lend to the trivalent compounds of the latter a single one of the properties of the rare earths. We must seek the influence to which their character is due far over at the edge of the table.

In the foregoing pages no attempt has been made to criticise the analogies which exist, in the various series, between the elements themselves. With this feature of the system, little fault can be found. The alkali metals, the alkaline earth metals, Be, Mg, Zn, .:, Ge, Sn, Pb, are thoroughly similar among themselves, and well illustrate the gradation in properties with increasing atomic weight. But with the compounds the case is entirely different. The derivatives of typical elements show no regularity—even in their abnormal behaviour; the compounds of the 8th group have a decidedly anomalous position. The similarity between the derivatives of elements in states of oxidation uncalled for by the system, either cannot be explained at all, as in the case of lead and barium, magnesium and manganese compounds, or we are forced to ascribe to one or the other series a certain vague transitive nature. The reason for this lies, not in the principle that the chemical nature of an element and its compounds is a function of its atomic weight, but in our failure to recognise the two-fold character of this principle. We attempt to apply one and the same expression of the law to both elements and compounds. But one has no right, in the systematisation of one class of substances, to impose upon himself restrictions which arise only from the system which he employs for another class. No arrangement of the elements according to their atomic weights can be made which expresses the analogies between the elements themselves, and in which, for instance, magnesium and manganese receive analogous positions. And the result is that, in order to emphasize the relation between zinc and magnesium which such an arrangement does exhibit, the adherent of the periodic system deliberately closes the door to an explanation of the far closer analogy between the compounds of magnesium and manganese, as if the latter were not conditioned by an equally important law of nature.

A system for the compounds, founded upon the atomic weights of the elements must also necessarily lead to confusion from another source, for the investigation of the compounds is undertaken solely to characterise the *general chemical nature* of the element. Thus, little distinction is drawn between reactions which do not involve a change in the degree of oxidation and those which do. If the two are separated at all, it is only when the resulting compounds are very stable, or else conform to the position of the element in the periodic system. To cuprous compounds, though they are unstable, great importance is attached, because copper belongs to the first family. But, even in so full and scientific a text-book as that of Mendeleeff, the salts of trivalent manganese are reviewed with little more than the passing remark that they somewhat resemble ferric compounds, and that the chloride decomposes when its solution is warmed. The latter fact seems to deprive the manganic salts of all theoretical interest.

But in a comparison between the derivatives of two metals in the same degree of oxididation, the question of *existence* becomes of more importance than stability, for the latter is often dependent entirely upon external conditions. The fact that bromine is liquid, iodine a solid, at ordinary temperatures, does not prevent the most important analogies being drawn between the physical properties of the halogens in the same state of aggregation, though to obtain bromine and iodine as gases, heat must be employed. So it is with many compounds. They may perhaps be obtained only under, for us, extraordinary conditions, but their very existence may point out in the constituent elements properties which we should otherwise never expect. As an example of such a case only the newly discovered alums of vanadium need be mentioned. The existence of these bodies shows that in spite of the similarity between phosphates and vanadates, the vanadium atom exerts upon the nature of its trivalent compounds the same influence as does iron upon that of the ferric salts. A vanadic solution absorbs oxygen with great avidity, and is therefore called very unstable, but the presence of oxygen is an arbitrarily imposed condition. If oxygen were a rare element, the trivalent salts of vanadium would probably be regarded as its normal compounds, and a vanadate looked upon very much as we look upon ferric acid to-day.

The chemical behaviour of an element in a given degree of oxidation must be characterised along two lines. First, by the study of its compounds as mineralogical specimens, their composition, physical properties, solubility, volatility, and the like, together with the reactions which they show without involving change in the degree of oxidation. Secondly, by its passage from this degree of oxidation into others. The first is, in my opinion, by far the more important, for the properties of the compounds of an element in two different degrees of oxidation differ absolutely from one another; and in the two the element appears in entirely different rôles. It is only after we have ascertained in how far the element can alter its *apparent* character, in corresponding with entirely different elements in different degrees of oxidation, that we can solve its *true* character, and find out a general law for its behaviour in all its compounds; and this can be ascertained only by a careful comparison of its compounds with those of other elements in the same degree of oxidation.

A classification based upon this principle, of course, presents great difficulties, owing to the very unsatisfactory extent to which the elements in their unstable degrees of oxidation have been investigated. A thorough study of the compounds, however, has shown that it is capable of giving most interesting results, the nature of which I will discuss in my next article on the subject.

PRELIMINARY REPORT OF THE COMMITTEE ON COAL ANALYSIS.*

At the Cleveland meeting of the American Chemical Society a Committee, consisting of W. F. Hillebrand, C. B. Dudley, and W. A. Noyes, was appointed to consider the methods of proximate analysis of coal with a view to the adoption, if possible, of uniform methods for this country. After discussion among themselves, the committee have formulated the following outline of methods for analysis which they herewith submit, rather as a means of securing further information than as a final report. The committee very earnestly request all chemists interested in the matter, who may see this report, to send to the chairman of the committee a criticism of the methods proposed and a statement of any objections they see, and of any modifications which they think desirable.

Since the literature of the subject is widely scattered and much of it is not easily accessible, the committee request that all who have published papers bearing on the subject will, if possible, send to the committee reprints of such papers, or, if that cannot be done, a statement of where such papers can be found and the points covered.

Without the full and hearty co-operation of others, the labours of the committee will be greatly increased, and the conclusions finally arrived at will be less representative of general experience than it is desired they should be.

Methods of Analysis.

1. *Sampling.*—At least 5 pounds of coal should be taken for the original sample, with care to secure pieces that represent the average. These should be broken up and quartered down to obtain the smaller sample which is to be reduced to a fine powder for analysis. The quartering and grinding should be carried out as rapidly

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* From the *Journal of the American Chemical Society*, xx., No. 4.

as possible, and immediately after the original sample is taken, to prevent gain or loss of moisture. The powdered coal should be kept in a tightly stoppered tube or bottle till analysed.

2. *Moisture.*—Dry 1 grm. of the coal in an open porcelain or platinum crucible at 104—107° for one hour, best in a double-walled bath containing pure toluene. Cool in a desiccator and weigh covered.

Question: Has anyone experience with other methods of drying? over sulphuric acid, *in vacuo*, in a current of air, in watch-glasses, or otherwise? Especially in this and other cases the committee desire any comparative results which can be furnished.

The following comparison of the effect of drying one hour in toluene bath, twenty hours *in vacuo* over sulphuric acid, and in air over sulphuric acid was made by Dr. Hillebrand.

		One hour in toluene bath.	Twenty hours *in vacuo* over H_3SO_4.	In air over H_2SO_4.		
				2 hrs.	48 hrs.	120 hrs.
Coal No. 1	..	2·85	3·60	2·87	3·15	3·39
,,	..	3·10	3·59	—	—	—
,,	..	3·23	3·57	—	—	—
,,	..	3·25	3·49	—	—	—
,,	..	3·24	—	—	—	—
,,	..	3·22	—	—	—	—
,,	..	3·27	—	—	—	—
Coal No. 2	..	1·84	2·08	1·77	—	2·00
,,	..	1·83	2·07	—	—	—
Coal No. 3	..	1·52	1·75	1·42	—	1·70
,,	..	1·51	1·73	—	—	—
Coal No. 4	..	1·01	1·04	1·05	—	1·18
,,	..	1·08	1·03	—	—	—
Coal No. 5	..	1·40	1·69	1·45	—	1·66
,,	..	1·41	1·67	—	—	—
,,	..	—	1·67	—	—	—
Coal No. 6	..	0·30	0·21	0·23	—	0·25
,,	..	0·34	0·28	—	—	—

These results seem to indicate that drying *in vacuo* gives higher, and probably more correct, results than drying at 105° for one hour.

The following experiments were carried out by Mr. W. E. Burk at the Rose Polytechnic Institute (see *Proc. Indiana Acad. of Sciences*, 1896, p. 113) for the purpose of determining whether volatile matter other than water is lost in drying bituminous coals. A hard glass tube was partly filled with copper oxide, partly jacketted with a glass sleeve so that a portion could be heated to 100° by a current of steam. The coal was weighed in an aluminum boat enclosed in a weighing tube, and was then heated to 100° for an hour in a current of dry air. The moisture and any volatile matters which were expelled were passed over the heated copper oxide and the water and carbon dioxide were absorbed as usual in calcium chloride and in potash bulbs. The results were as follows:—

Weight of coal taken.	Loss in weight of coal at 100°.	Water found in calcium chloride tube.	Per cent of water in coal.	Per cent of carbon found in potash bulbs.	Per cent of excess of hydrogen found.
1·4217	0·1994	0·2014	14·00	0·048	0·016
1·1195	0·1596	0·1625	14·25	0·058	0·029
3·1079	0·2111	0·2113	6·78	0·022	0·001
3·2356	0·2152	0·2142	6·65	0·025	—
2·9408	0·1967	0·1967	6·65	0·037	—

The amount of moisture found was slightly higher than was found in the same coal by the usual method, perhaps because of the current of dry air over the coal. Since the loss of volatile matter other than water was always less than one-tenth per cent, it can safely be disregarded for most practical purposes with coals of this class.

3. *Volatile Combustible Matter.*—Place one grm. of fresh undried coal in a platinum crucible, weighing 20 to 30 grms. and having a tightly fitting cover. Heat over the full flame of a Bunsen burner for seven minutes. The crucible should be supported on a platinum triangle with the bottom 6 to 8 c.m. above the top of the burner. The flame used should be 20 to 25 c.m. high when burning free, and the determination made in a place free from draughts. The upper service of the cover should burn clear, but the under surface should remain covered with carbon. To find "Volatile Combustible Matter," subtract the per cent of moisture from the loss found here.

Questions: Should a larger portion be taken? Should the coal be heated more gradually at first? Should a blast be used? Can results be obtained by heating in a muffle, or in any other manner, which will agree with those obtained by this method?

The committee consider the determination as largely arbitrary, in any case, and believe that uniform results in the hands of different chemists will be best secured by making the conditions as simple as possible. The most serious objection to the method proposed appears to be the danger of mechanical loss at the commencement of the heating. It is believed, however, that the error from this source is less than would arise from any method which leaves the application of the heat to the judgment of the operator.

The committee especially desire to secure any analytical data which may be available to show the degree of concordance of results obtained by the same or different chemists, Also any comparison of analytical results with results of commercial coking.

4. *Ash.*—Burn the portion of coal used for the determination of moisture, at first over a very low flame, with the crucible open and inclined, till free from carbon. If properly treated, this sample can be burned much more quickly than the dense carbon left from the determination of volatile matter.

Question: Are carbonates likely to be present in the ash in such amount that heating over a blast would lessen the weight appreciably?

When the sulphur in the coal is in the form of pyrites, that compound is converted almost entirely into ferric oxide in the determination of the ash, and, since three atoms of oxygen replace four atoms of sulphur the weight of the ash is less than the weight of the mineral matter in the coal by five-eighths of the weight of the sulphur. While the error from this source is sometimes considerable, the committee is not now prepared to recommend such a correction.

5. *Fixed Carbon.*—This is found by subtracting the per cent of ash from the per cent of coke as found in paragraph 3.

6. *Sulphur.*—What methods are used? Eschka's, with sodium or potassium carbonate, fusion with sodium carbonate and potassium nitrate, Carius's or others? Any comparative results are especially desired.

7. The committee would recommend that the heating effect be calculated on the basis of the coal burned to carbon dioxide and vapour of water at 100° C., and be stated either in calories per kilogrm. or English heat units per pound. The theoretical evaporative effect is to be calculated by dividing the number of calories per kilogrm. by 536, or the number of English heat units per pound by 965. In either case it expresses the theoretical number of kilogrms. or pounds of water converted into steam from and at 100° C. by one kilogrm. or pound of the coal.

A calculation of the results of 21 analyses, and determinations of heating effect with the bomb calorimeter, made with Indiana and Pittsburg bituminous coals, shows that the heating effect may be found in all cases examined, with a maximum error of 2 per cent, by the following rule:—

Subtract from 100 the per cents of moisture and ash and one-half the per cent of sulphur, and multiply the remainder by 80·7. The product will be the heating effect of the coal burned to vapour of water, expressed in calories.

The committee will be glad of any data which will enable them to further test this factor, and also of any data with regard to other methods of determining heating effect.

Persons interested in the subject of coal analysis are requested to send any communications they may wish to make to Prof. W. A. Noyes, Rose Polytechnic Institute, Terre Haute, Ind.

W. A. Noyes,
C. B. Dudley,
W. F. Hillebrand, } Committee.

February 22, 1898.

A REDUCTION OF PERMANGANIC ACID BY MANGANESE PEROXIDE.*

By H. N. MORSE and C. L. REESE.

In a previous article (*Am. Chem. Journ.*, xviii., 401), one of us, together with Messrs. Hopkins and Walker, described certain experiments on the reduction of permanganic acid by percipitated manganese peroxide. It was there concluded that, whenever the latter is introduced into, or is formed in the presence of, the former or its salts, a reduction of the acid occurs with an evolution of three-fifths of its active oxygen, in accordance with the following equation—

$$xMnO_2 + 2HMnO_4 = (x + 2)MnO_2 + H_2O + 3O.$$

It was also shown that to this cause is to be ascribed the observed instability of solutions of permanganate.

Six months later (*Ber. d. Chem. Ges.*, xxix., 2549), there appeared an article by Messrs. V. Meyer and Max Von Recklinghausen in which is described the evolution of oxygen which takes place when hydrogen or carbon monoxide is absorbed by a nearly saturated (5 per cent) acidified solution of potassium permanganate. The opinion was then expressed by one of us (*Ibid.*, xxx., 48), that the phenomenon observed by Messrs. Meyer and Von Recklinghausen was due to the peroxide which is formed when reducing gases are absorbed by permanganic acid; in other words, that it is an instance of a kind of reaction which had been under observation in this laboratory for several years.

After the communication referred to had left the hands of the author, but before it appeared in printed form, an article by Messrs. H. Hirtz and V. Meyer was published (*Ber. d. Chem. Ges.*, xxix., 2828), in which they maintain that the phenomenon observed by Messrs. Meyer and Von Recklinghausen is fundamentally different from that described by Morse, Hopkins, and Walker. The grounds for this opinion appear to be two-fold. In the first place the authors make the wholly unwarranted assumption that Morse, Hopkins, and Walker experimented with *neutral* solutions only, that is, with potassium permanganate; while Messrs. Meyer and Von Recklinghausen employed *acidified* solutions. We cannot interpret otherwise the expressions: " Diese Forscher haben gefunden dass eine Loesung von uebermangansaurem Kali unter gewissen Bedingungen durch fein vertheilten Braunstein unter Entwickelung von Sauerstoff zersetzt wird." . . . " Da nämlich Wasserstoff und Kohlenoxyd als reducirende Koerper aus der Loesung der uebermangansäure Braunstein ausscheiden, und dieser, nach den genannten Autoren, mit Kaliumpermanganat Sauerstoff unter gewissen Bedingungen entwickeln kann." . . . "Ob nun die Morse-Hopkins-Walker'sche Erscheinung bei unseren *Säure*-loesungen eintrete." . . . How erroneous must have been the view which we ascribe to Messrs. Hirtz and Meyer, on the basis of the above quotations, will appear when we state that, of the forty-eight experiments described by Morse, Hopkins, and Walker, thirty-five were with *acidified* solutions of permanganate.

The second ground which the authors have for believing that the evolution of oxygen observed by them is not due to the action of the oxide on the permanganic acid, is one of great weight, but, to our minds, it is by no means conclusive. They found that when hydrogen, or carbon monoxide, is absorbed by a 5 per cent solution of potassium permanganate to which has been added 2·5 volume-per cent of concentrated sulphuric acid, the evolution of oxygen which occurs *during the absorption* is much more rapid than that which takes place *after the exhaustion* of the gas. This was shown in the following manner: 20 c.c. of the acidified permanganate solution and 40 c.c. of hydrogen were inclosed in a glass-tube and agitated together for twenty-four hours. The tube was then opened and the gas in it displaced by carbon dioxide. On closing the tube again and agitating the contents for another twenty-four hours it was found that only 2·5 c.c. of oxygen had been liberated, whereas, according to the experience of Messrs. Meyer and Von Recklinghausen, about 20 c.c. of oxygen are evolved when, under similar conditions, 20 c.c. of the permanganate solution and 40 c.c. of hydrogen are agitated for the same length of time, or even for a shorter time.

It is clear then—and our own results, to be given hereafter, confirm the conclusion—that the evolution of oxygen, which occurs when a gaseous reducing-agent is being absorbed by a concentrated acidified solution of permanganate, is much more rapid than that produced by the oxide, which results from the absorption after the gas has disappeared. It is also more rapid than that observed when an equivalent amount of oxide is produced in the permanganic acid by a liquid reducing-agent, like a solution of manganous sulphate. To us, however, the conclusion that the evolution of oxygen in the two cases is due to wholly different causes is not obvious. We should suspect, rather, that the great initial evolution, observed when hydrogen and carbon monoxide are absorbed, is in some way dependent on the *gaseous* character of these reducing-agents.

We know at present altogether too little regarding the reduction of permanganic acid by the peroxide to give an opinion of any value as to its cause; and we attach very little value to present speculations on the subject, except so far as they may prove useful in giving direction to a further study of the phenomenon. There is, however, one fact which suggests a provisional hypothesis. We have considerable evidence tending to show that the molecules of the ordinary precipitated peroxides of manganese are quite complex. Perhaps the best evidence of this is to be found in the large formulæ which must be assigned to them in view of the small proportions of water, or of alkalis or other bases which they contain. If they are thus complex, it is conceivable that the tendency toward increasing complexity of constitution should be strong enough to effect the decomposition of permanganic acid with liberation of the superfluous oxygen.

If, in the absence of any other explanation the reduction of permanganic acid by the peroxide, we accept for the moment the proposed hypothesis, we should ascribe the greater inital evolution of oxygen which is observed when gaseous reducing-agents are used, to the greater initial simplicity of the precipitated peroxide molecules. It is interesting in this connection to notice the volume-relations of the hydrogen absorbed and the oxygen which is liberated during or immediately following the absorption. They are approximately 2 : 1 in all of the experiments of Meyer and Von Recklinghausen. This relation would be explained in terms of the suggested hypothesis by the following reactions:—

$$2HMnO_4 + 3H_2 = 4H_2O + 2MnO_2;$$
$$2MnO_2 + 2HMnO_4 = H_2O + 2(MnO_2)_2 + 1\tfrac{1}{2}O_2.$$

We wish to state again that we have but little confidence in the above speculations. We claim for this merit only, that, inherently, they are not less improbable than the supposition that the evolution of free oxygen in the two cases under consideration is due to entirely distinct and different causes.

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* From the *American Chemical Journal*, xx., No. 7.

Furthermore, we do not see that the problem can be solved by any simple experimental demonstration. The "experimentum crusis" of Messrs. Hirtz and Meyer (*Ber. d. Chem. Ges.*, xxix., 2829), established but one thing; namely, the fact that the evolution of oxygen is phenomenally rapid during or immediately subsequent to the precipitation of the peroxide when a gaseous reducing-agent is employed, and that fact, taken alone, appears to throw no light on the cause of the evolution. Convinced that, with our slight bases of established fact, discussion is premature, if not profitless, we have undertaken a further study of the reduction of permanganic acid by manganese peroxide. The present communication contains the results which were obtained on treating the acid, under equal conditions, with equivalent quantities of hydrogen gas and manganous sulphate. We have thus far experimented with three concentrations of permanganate solution.

The first (A) contained in 1 c.c. 2·822 miligrms. of $KMnO_4$ equivalent to 5 milligrms. of iron. The second (B) was twice as concentrated as A. The third (C) contained in each c.c. 51$^{2}_{-}$ milligrms. of $KMnO_4$, equivalent to 90·38 milligrms. of iron. The solutions A and B are of the concentration usually employed in analytical work, while C has about the strength of the 5 per cent solution which was employed by Messrs. Meyer and Von Recklinghausen and later by Messrs. Hirtz and Meyer.

Great pains were taken to free these solutions from the oxide which is usually found in the commercial salt, and which, as has been shown, is the usual cause of the instability of unfiltered solutions of potassium permanganate. To this end compact abestos filters were prepared upon perforated porcelain disks placed in the bottom of cylindrical funnels, such as are used in the Gooch method of filtration. Two filters, one placed above the other, were employed. The lower one was closed with a perforated stopper through which the stem of the upper one passed. The filter through which the liquid entered the flask was thus protected from the dust of the air, and the absence of any brown colouration of the lower filter proved the effectiveness of the filtration. We have found these precautions necessary in all quantitative experiments on the reduction of permanganic acid by the peroxide; since, if they are neglected, it is impossible to ascertain how much of the observed reduction is to be ascribed to the oxide purposely added, and how much to that which was already in the solution.

When solutions of permanganate which contain suspended oxide are heated—especially those which have been acidified—the quantity of the oxide increases very rapidly. We call attention to this fact in connection with the necessity for careful filtration, because it appears to us to have a bearing on some of the results which were obtained by Messrs. Meyer and Von Recklinghausen. Their acidified solutions were "gut ausgekocht," but it does not appear from their published account that they were filtered.

The volume of permanganate solution used was the same in all experiments; namely, 20 c.c. This quantity was enclosed with whatever was to be added to it, in tubes having about 80 c.c. capacity, except in the case of solution C, where, owing to the large volume of hydrogen used in some experiments, larger tubes were employed.

Our agitating arrangement was an oscillating table upon which the tubes were held by rawhide lacings. The table was rocked by means of an electric motor and made about 100 strokes per minute. The agitation was continuous, except for occasional interruptions which lasted only a few minutes.

The amount of reduction effected during the agitation was measured by means of standard solutions of oxalic acid and potassium permanganate. This method, with the use of calibrated measuring apparatus, appeared to us quite as accurate as that of determining directly the volume of the liberated oxygen.

Messrs. Meyer and Von Recklinghausen found that when 20 c.c. quantities of their 5 per cent acidified solution of permanganate were agitated with air in closed tubes, they obtained volumes of oxygen ranging from 1·9 to 2·9 c.c. An agitation of thirty-three and a half hours gave them 1·9 and 2·2 c.c., while in a parallel experiment in which the agitation was continued for eighty-seven hours they obtained only 2·4 c.c. In another instance the volumes of liberated oxygen were, at the end of thirty-three and a half hours 2·8 and 2·9 c.c., and at the end of eighty-seven hours 2·4 c.c. Since the decomposition was not appreciably greater in eighty-seven than in thirty-three and a half hours the authors were led to believe that there is a limit to the reaction by which the oxygen is liberated. These results were not in accord with our own experience. In the first place, we have always found dilute, moderately acidified solutions of permanganate quite stable at ordinary temperatures, provided they were free from oxide. In the second place, in all the cases which have come under our observation, the decomposition of permanganic acid by the peroxide, which is attended by the liberation of oxygen, has been a continuous reaction, which ceased only when all of the acid had been reduced to the oxide. We had not, however, experimented with solutions as concentrated as that used by Messrs. Meyer and Von Recklinghausen. We therefore inclosed in glass tubes of about 80 c.c. capacity 20 c.c. portions of permanganate solution C. (51 milligrms. of $KMnO_4$ per c.c.) and volumes of diluted sulphuric acid, which were equivalent to three times the potassium of the salt. These were agitated for twenty-four hours and then titrated with oxalic acid. The reduction, if any had taken place, was too minute to be detected, nor was any trace of a brown deposit upon the glass to be discovered. The degree of acidity was somewhat greater in our solution than in that employed by Messrs. Meyer and Von Recklinghausen. The difference in the results we must ascribe to the absence of oxide from our solution, and the presence of it in theirs. Their 5 per cent solution of permanganate was acidified with *concentrated* acid, and then boiled ("gut ausgekocht"), but it does not appear to have been filtered. This treatment leads infallibly to the formation of a large quantity of the oxide; for, when strong sulphuric acid is added to a 5 per cent solution of the salt, there is a visible precipitation of the peroxide, and the quantity of it is rapidly increased by heating the solution to the boiling-point. Our solution, on the other hand, was filtered with great care, and acidified with diluted acid (3 parts of water to 1 of acid). Moreover, great pains were taken in cleansing the tubes, and to prevent the entrance into them of dust, or any reducing substance.

Having failed to establish the fact of decomposition within twenty-four hour periods, we determined to extend the time of agitation, using varying proportions of acid; and to compare the more dilute solutions A and B with C with respect to stability. The results, and the conditions under which they were obtained, are given in tabular form. The numbers given under the head of "volume reduced" signify reduction in accordance with the equation $2HMnO_4 = H_2O + 2MnO_2 + 3O$, and not total reduction of the permanganic acid. (See next column).

It will be seen that none of the three solutions in the neutral condition lost a measurable quantity of oxygen. As regards the acidified solutions, it appears that A and B suffered but little, if any, decomposition, whether the acid was equivalent to once or six times the potassium of the permanganate. In the case of those acidified portions of the solution C, in which the acid was equivalent to three times the potassium of the permanganate, there was, after an agitation of one hundred and fifty hours, some evidence of decomposition. A slight deposit of the brown oxide could be detected upon the glass. This evidence of reduction was wanting in those instances in which the acid was equivalent to once and twice the potassium.

If we succeeded in our endeavour wholly to exclude the oxide from our solutions, it must be concluded that a 5 per cent solution of permanganate becomes *per se* some-

Permanganate Solution A ; 1 c.c. = 5 M.grms. Fe.

Acid.	Time. Hours.	Volume reduced. C.c.	Oxygen lost. C.c.
O	300	0·12	0·06
O	300	0·11	0·05
=K	300	0·11	0·05
=K	300	0·06	0·03
=2K	300	0·20	0·10
=2K	300	0·10	0·05

Permanganate Solution B ; 1 c.c. = 10 M.grms. Fe.

O	150	0·02	0·02
O	150	0·04	0·04
=3K	150	0·10	0·10
=3K	150	0·10	0·10
=6K	150	0·08	0·08
=6K	150	0·10	0·10

Permanganate Solution C ; 5 per Cent $KMnO_4$.

O	150	0·00	0·00
O	150	0·00	0·00
=K	150	0·05	0·45
=K	150	0·04	0·36
=2K	150	0·02	0·18
=2K	150	0·11	0·99
=3K	150	0·40	3·61
=3K	150	0·22	1·91

what unstable when treated with a quantity of sulphuric acid which is equivalent to three times the potassium of the salt. Our solution C, however, proves itself much more stable than the equally concentrated, but somewhat less acid, solution of Messrs. Meyer and Von Recklinghausen. The most obvious cause of this difference we have already referred to, namely, the certain presence of suspended oxide in their solution at the beginning of the agitation.

We shall not attempt to explain the fact that Messrs. Meyer and Von Recklinghausen obtained no larger volumes of oxygen after an agitation of eighty-seven hours than were liberated in other experiments during thirty-three and a half hours; but it occurs to us as something which may have a bearing on the case, that unless proper precautions were taken at the time of transferring the liquid to the tubes, to secure a uniform distribution of all the suspended and precipitated oxide, the quantities of oxide introduced into the different tubes would be likely to vary. That the liberation of oxygen, which occurs when an acidified solution of permanganate containing suspended oxide, is agitated in closed tubes, *does not* cease after a few hours will be amply proved by our later experiments.

(To be continued).

SOME PRINCIPLES AND METHODS OF ANALYSIS APPLIED TO SILICATE ROCKS.*

By W. F. HILLEBRAND.

(Continued from p. 66).

Silica, Alumina, &c.

Remarks on alternative Methods of Decomposition.—Various fluxes other than alkaline carbonates have been recommended for breaking up silicates insoluble in ordinary acids, such as lead and bismuth oxides, lead carbonate, borax, and boric acid. Prof. P. Jannasch and his pupils have been especially active of recent years in this line of work, as evidenced by their numerous published papers. One of the advantages these fluxes possess over the alkaline carbonates is their removability after serving their purpose, thus allowing the various separations to be made more perfectly and without the annoying interference of several grms. of foreign fixed salts, which are most troublesome in that part of the analysis devoted to the separation of silica, alumina, iron, lime, and magnesia.

Another of their advantages is that with some of them it is possible to estimate in one portion the alkalies, in addition to those constituents usually determined in the silica portion. Where the material is limited, as it so often is in mineral analysis, this is a most important advantage, sufficient to outweigh all possible objections; but in rock analysis, where the supply of material is usually ample, it is rarely worth considering. A still further point in their favour is, that it is probably more easy to obtain them entirely free from fixed impurities than an alkaline carbonate.

There are, however, objections to their use. With some of them an extraordinary amount of time must be devoted to grinding the mineral to an impalpable powder, and the flux itself may need considerable hand pulverisation. Once introduced, they must be removed before the analysis can be proceeded with, and this removal takes much time and is always a possible source of error. The expulsion of boric acid and drying of the silica in the recent method of Jannasch and Heidenreich (*Zeitsch. fur Anorg. Chemie*, xii., p. 208, 1896), from their own account requires the almost constant supervision of the chemist for several hours. In mineral analysis these objections are entitled to far less weight than in rock analysis, since the object sought—usually the deduction of a formula—warrants the expenditure of much time and painstaking care. Finally, it has been found that one or more of these fluxes are not available for altogether general use, since certain minerals do not fully succumb to their attack, as andalusite with boric acid and others with lead oxide (Jannasch). Therefore, however well adapted one or the other of these methods may be for the analysis of homogeneous minerals, it is very improbable that the vivid anticipations of Prof. Jannasch (*loc. cit.*, p. 219), to the effect that the boric-acid method will soon supersede the alkaline-carbonate-fusion method in rock as well as mineral analysis, will be speedily realised. Nor can the great saving in time of 50 per cent which is claimed be for a moment admitted. It may be that a chemist attending to only one analysis at a time will finish it somewhat sooner by following Prof. Jannasch's procedure than the one here outlined; but it is quite possible, as previously intimated, for two—or even sometimes portions of three—analyses to be carried on in different stages of completion at the same time by the methods herein set forth.

The practice of separating alumina, &c., by the usual methods, after first attacking the rock powder by hydrofluoric and sulphuric acids—silica being estimated in a separate portion—while attractive in principle, was abandoned by the writer after fair trial, owing to the disturbance sometimes occasioned by incomplete expulsion of fluorine and to a less degree by the presence of sulphates instead of chlorides. With exception of the comparatively few analyses made thus, the sodium-carbonate method has always been employed. In the case of rocks rich in fluorine strict accuracy would require the separation of silica to be made as in the Berzelian method for fluorine estimation; but in practice it is hardly ever necessary to resort to this tedious procedure, since the amount of fluorine is usually small, and it can by no possibility cause a loss of much more than three-fourths its own weight of silica by volatilisation as silicon fluoride when the sodium-carbonate fusion is evaporated directly with hydrochloric acid. Probably the loss is less, since some fluorine perhaps escapes as hydrofluoric acid. However this may be, the error is of comparatively slight importance, since it attaches to the constituent always present in greatest amount.

Purity of the Sodium Carbonate used as a Flux.—Notwithstanding the most earnest efforts for years, it has been impossible to procure, either in the open market or

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* From the *Bulletin of the United States Geological Survey*, No. 148, p. 15, 1897.

by special arrangement with manufacturers, an article of sodium carbonate which can be called chemically pure. With special precautions small lots can be prepared in the laboratory that will contain less than 1 m.grm. total impurity in 10 grms.; but such an article cannot be purchased in the market, and rarely will the so-called chemically pure dry sodium carbonate contain as little as 1 m.grm. in 10 grms. The invariable contamination, aside from sand and straw, which have sometimes been found in large amount, is silica, alumina, iron, lime, and magnesia, all of these going into aqueous solution with the carbonate. The chief of these impurities are usually silica, alumina, and lime. An article of the above degree of purity is satisfactory in almost all imaginable cases, since the use of the usually extravagant amount of 10 grms. for a fusion would introduce an error of but 0·1 per cent in the analysis, supposing 1 grm. of mineral to be operated on. This error is undoubtedly fully equalled by the introduction of dust from the air in the various long evaporations.

Precautions in Fusing.—Special directions with regard to the fusion and its first treatment are unnecessary, except to say that the flame should not be directed vertically against the bottom of the crucible, but at an angle against the side and bottom, nor should the flame be allowed to envelop the whole crucible. These precautions apply in all ignitions of reducible substances, and yet they are rarely observed. In neither case, if neglected, will there be the necessary oxidising atmosphere within the crucible; on the contrary, reduction may occur fraught with serious consequences. This is especially true if the rock contains more than traces of pyrite or other sulphide, when, after cleansing and igniting the crucible, there may appear on its interior a darkening due to oxidation of reduced iron which had alloyed with the platinum. This may in exceptional cases amount to several m.grms. in weight, and can be removed only by repeated ignitions, followed each time by scouring or treatment with hydrochloric acid. In order to avoid the use of nitre in case of pyritiferous rocks, it is well to first roast the weighed powder in the crucible in which the fusion is to be made.

It sometimes happens that the cooled flux, and even its solution, will indicate absence of manganese when it is really present in quantity to give normally a strong colouration. Two fusions made side by side or successively, under apparently similar conditions, may in one case show little or no manganese; in the other considerable. This observation has been frequently made, and therefore the absence of a bluish-green colour in the fusion is not to be taken as proof of the absence of manganese. This difference of behaviour I can ascribe to no other cause than that of a reducing atmosphere in one of the crucibles and an oxidising one in the other, even though the conditions were apparently alike.

Drying and Testing of Silica.—As to the best way of rendering silica insoluble by evaporation, my own predilection is for a double evaporation instead of a single one on the water-bath. By fusing with sodium carbonate in the forenoon, the silica is ready for the first filtration in the afternoon. It is quite unnecessary to carry the evaporation beyond approximate dryness. The filtrate is again evaporated, always in platinum, and is ready for final filtration the following morning, when approximately 1 per cent of silica is recovered and added to the main portion. My experience is that a better separation of silica is effected hereby, and in no more time than by a single long evaporation. That which is subsequently recovered from the ammonia precipitate rarely exceeds a half, or, at the most, 1 m.grm.

Drying in an air-bath at 110° C. or higher, or on a hot plate or sand-bath, or over a free flame, in order to render silica insoluble, offers no advantage unless much magnesium is present, and then the most favourable temperature, according to Gilbert (*Technology Quarterly*, iii., p. 61, 1890; Abstract in Fresenius's *Zeitschr. fur Anal. Chemie*, xxix., p. 688, 1890), is 120° C. The presence of much calcium chloride seems to facilitate dehydration of the silica, while magnesium chloride above 120° C., by decomposing, forms a silicate which dissolves in hydrochloric acid and increases the amount of silica carried into the filtrate. It does not appear from Gilbert's paper that the blast-furnace slags, on which he experimented, contained titanium, phosphorus, or iron in appreciable amounts. Basic magnesian rocks usually do, and in such cases it is doubtful if the employment of a drying temperature of 120° would not materially add to the large impurity always to be expected with the silica. In other cases he confirms the earlier belief that drying temperatures higher than that of the water-bath increase the amount of insoluble impurity, chiefly alumina, in the silica, and that this amount cannot be reduced by long digestion with hydrochloric acid. Further, he confirms Lindo's statement that evaporation with sulphuric acid till the appearance of white fumes gives a higher result in silica than with hydrochloric acid. But for general rock analysis the use of sulphuric acid at this stage must be rejected utterly.

Blasting for twenty to thirty minutes is necessary to expel all moisture from the silica. Its weight should always be corrected for impurities, which are never absent, by evaporating with hydrofluoric and sulphuric acids and again blasting. If toward the end of evaporation with these acids, when the hydrofluoric acid has been driven off and the sulphates begin to appear in solid form, the residue has a peculiar milky or enamel-like appearance, it may be taken as evidence of much phosphorus and titanium.* This appearance is so unusual and striking that it is worth while calling attention to it. With basic rocks very rich in titanium and phosphorus the residue may amount to 2 or even 3 per cent of the rock.

The subsequent precipitate of alumina, &c., is usually ignited in the crucible containing the residue from the silica.

It might be supposed that this residue would contain most of the barium of those rocks carrying that element together with sulphur or sulphates, but the reverse is true as a rule. Only when there is a considerable excess of SO_3 over the BaO will much of the latter be found there, and usually there is none at all. Should some be present, its removal and estimation at this stage is not necessary, as it can be more conveniently recovered later, together with the silica accompanying the alumina, &c., precipitate.

The separation of silica in rocks containing fluorine has been touched upon in commenting on the sodium carbonate method of fusion.

Platinum in Filtrates.—The filtrates from the silica always contain notable amounts of platinum. This arises in very small degree from the crucible fusion, in a larger one from the action of hydrochloric acid on manganate and permanganate, sometimes chromate of sodium, and, if much iron is present, in no small degree from the reduction of ferric chloride to ferrous by the platinum of the dish. This reaction is little known, apparently, but is mentioned in Gmelin-Kraut (*Anorg. Chem.*, iii., p. 359, sixth revised edition), and can be readily demonstrated by evaporation of ferric chloride in platinum.

Metals of the Hydrogen Sulphide Group.—The presence in appreciable amounts of metals precipitable by hydrogen sulphide, except perhaps copper, is of such infrequent occurrence in most rocks that discussion is unnecessary in their connection. In case it is necessary to precipitate them, however, it is always well to bear in mind that some titanium may be thrown down along with them. Separations of the silica should be made in porcelain, to eliminate platinum, or, better still, the quantitative estimation of any of these metals should be made in a separate

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* It is possible that this appearance is caused by zirconium with the phosphorus and titanium. (See page 81, footnote).

portion of the rock broken up by the action of hydrofluoric and sulphuric acids.

Alumina, &c.—The removal of platinum from the filtrates before precipitating alumina and iron is quite unnecessary, and to do so would involve the re-oxidation of all iron and subsequent boiling to remove or destroy the excess of oxidising agent, together with the waste of much valuable time. The iron is already oxidised by the fusion, and needs no further help in that direction.

Two precipitations by ammonia are usually quite sufficient to separate iron, alumina, phosphoric acid, chromium, titanium, and zirconium, if all these are present, from nickel, manganese, the alkaline earths, and magnesium, provided ammoniacal salts are present in sufficient quantity. This last point is of special importance as regards magnesium, and failure to observe it is doubtless the reason why many old analyses and sometimes modern ones show utterly improbable percentages of alumina, especially as chemists were formerly often satisfied with a single precipitation. The necessary ammonium chloride is better obtained by the use of purified ammonia water and hydrochloric acid than by the addition of the solid salt, which is seldom pure.

Manganese not always separated by Ammonia.—But it will occasionally happen that the separation from even very small amounts of manganese is altogether incomplete, and the uncertainity of insuring this separation has led the writer of late to employ the basic acetate method for the first precipitation in all cases where manganese is present—and the exceptions are few—even though the precipitation of alumina is sometimes less complete than by ammonia.[*] Not more than 2, or at most 3, grms. of sodium acetate need be used. After slight washing the precipitate is re-dissolved in a sufficient excess of hydrochloric acid and re-precipitated by ammonia in slight excess. The complete boiling off of this excess is unnecessary, as pointed out by Genth and Penfield, since it is apparently the washing with pure water and not the free ammonia which carries small amounts of alumina into the filtrate. Penfield and Harper (*Am. Journ. Sci.*, Series 3, vol. xxxii., p. 112, 1886), recommend washing with a dilute solution of ammonium nitrate (20 c.c. nitric acid, neutralised by ammonia, to the litre), and also the solution of the first precipitate in nitric instead of hydrochloric acid, in order to shorten the washing, there being no chloride to remove.

The filtrates are strongly concentrated separately[†] in platinum, a drop or two of ammonia being added toward the end to the second one, and filtered successively through the same small filter into a flask of 150 to 200 c.c. capacity, the ammoniacal filtrate serving as wash water for the first dish and containing enough ammoniacal salt to prevent precipitation of magnesium in the first filtrate when mixed with it. If manganese has been deposited upon the surface of the dish it is removed by hydrochloric and a drop or two of sulphurous acids, which mixture is then passed hot through the filter. A re-precipitation by ammonia is then made, and the precipitate collected again on the filter and added to the main one, the filtrate passing into the flask containing the previous one. If much manganese is present, of course a second precipitation by ammonia, of the small precipitate, may be required. In these cases there is no difficulty in getting all the manganese into the filtrate.

Treatment of the Alumina Precipitate.—The combined alumina, &c., precipitates are ignited moist, in the paper, unless considerable iron is present, when the main one is dried, removed as far as possible from the paper, and the latter ignited separately to prevent partial reduction of a portion of the iron, which can not then be re-oxidised by heating (see *ante*).

Alumina in the quantities ordinarily found can not be fully dehydrated by the full heat of the Bunsen burner. It must be blasted for five or ten minutes. If iron is present in large amount this last operation must be conducted so as to ensure free access of air to the crucible (see *ante*).

Estimation of Silica and Iron in the Alumina Precipitate.—The precipitate is dissolved by fusion with acid potassium sulphate, an operation which is accomplished without trouble in from two to four hours if the temperature is kept low, and the acid salt has been properly made free from water and excess of acid. The melt is taken up with hot water and considerable dilute sulphuric acid, the residue collected, weighed, and corrected by hydrofluoric and sulphuric acids for silica, which, as said before, rarely amounts to 1 milligrm. in weight, and further examined for barium (see *ante*) by dissolving in hot, strong sulphuric acid and diluting with cold water.[*] The filtrate is reduced, hot, by hydrogen sulphide, boiled to collect the sulphur and platinum sulphide resulting from the bisulphate fusion, the hydrogen sulphide being allowed to pass for a short time after boiling[†] It is then filtered[‡] hot into a flask attached to a carbonic acid apparatus, and brought to boiling to expel hydrogen sulphide. When this is fully effected the flask is cooled in water while the carbon dioxide still passes, and the solution is then titrated by potassium permanganate. The results are strictly accurate when care is taken with the reduction by hydrogen sulphide, and the method is altogether superior to that of reduction by zinc, since no foreign impurity affecting the result is introduced, and the ever-present titanium is not also reduced. If this latter element has not already been tested for, its relative amount can be conveniently ascertained by adding hydrogen peroxide to the titrated ferric solution.

Alumina found by Difference.—In this laboratory titanium and phosphorus are estimated in separate portions, and likewise zirconium and chromium if present. The alumina is always found by difference after deducting their sum as oxides and the total iron as ferric oxide from the combined weights. This throws upon the alumina all errors involved in their separate determinations, but these may balance, and in any case the probable error can hardly be as high as that involved in the direct weighing of the alumina itself, considering the difficulty of effecting a satisfactory separation of it from all the

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[*] The fact must not be overlooked that certain of the rare earths may pass completely into the filtrate if the basic acetate method is followed. If then, later on, rendering the combined filtrates ammonical, an unexpectedly large precipitate appears, this should be carefully examined as to its nature. In an analysis of piedmonite from Maryland over 2 per cent of rare earths, including cerium and others not identified, were quantitatively separated in this way from iron, alumina, &c.

[†] If, instead of sodium acetate, ammonia alone has been used to precipitate alumina, &c., it has sometimes happened in the experience of others than the writer that on concentration of the first filtrate a pale pale straw-coloured precipitate appeared which remained on the filter with the traces of alumina that may also separate, although it is slowly soluble in hot water. This is some compound of platinum, and attention is called to it here for the guidance of others who may notice it and be unaware of its character.

[*] Some years ago, in a series of analyses of rocks from the Leucite Hills, in Wyoming, there was obtained at this stage, when it was customary to dissolve the melt in cold water only preliminary to precipitation of titanium by boiling the neutralised sulphuric solution in presence of sulphur dioxide, a white, more or less flocculent residue amounting to 1 to 3 per cent of the rock, which was at first taken to be a mixture of tantalic and columbic acids. Eventually it was found to consist apparently of nothing but TiO_2 and P_2O_5, with perhaps a little ZrO_2. By repeated fusion with acid potassium sulphate and leaching with cold water it could be gradually brought into solution. It was these rocks which furnished the most striking instance of the peculiar, milky, sulphate residues previously mentioned as derived from the ignited silica. Knop (*Zeit. für Kyrst.*, vol. x., p. 73, 1885) seems to have obtained a similar mixture in analysing minerals from the Kaiserstuhl in Baden, but its nature was not ascertained, though suspected to be, if not silica, coulmbiferous titanic acid.

[†] It may be mentioned that the precipitation of platinum from a hot sulphate solution is far quicker and cleaner than from hydrochloric acid.

[‡] Filtration is not necessary if only precipitated sulphur and no sulphides are in suspension, since this is without reducing action on cold permanganate solution, as Wells and Mitchell, and others before them, have pointed out. The above authors used this method of reducing ferric iron in titanic iron ores. (*Journ. Am. Chem. Soc.*, vol. xvii., p. 78, 1895; also Chemical News, vol. lxxiii., p. 123, 1896).

other admixtures, an operation which would, moreover, immoderately extend the time required for each analysis.

Alternative Method.—Should it be desirable for any reason to effect an actual further separation, this may best be done, up to a certain point, after the bisulphate fusion, by removal of the iron by ammonium sulphide in ammonium-tartrate solution, evaporation of the filtrate, ignition of the residue with sodium carbonate and nitrate, and extraction with water, whereby titanium and zirconium are left on the filter as sodium salts, and the chromium is carried into the filtrate as chromate. The further separation of Al_2O_3 and P_2O_5 from the chromium is outlined under the head of "Chromium." This is as far as the separation can well be carried, and the alumina must still be found by subtracting the P_2O_5 from the combined weights of the Al_2O_3 and P_2O_5. The possibility of loss of some P_2O_5 by volatilisation* during the bisulphate fusion must be borne in mind here, for if it takes place the final weight of Al_2O_3 and P_2O_5 will not contain all the P_2O_5.

Some writers recommend dissolving the ignited alumina, &c., in hydrochloric acid, but when the precipitate has been heated over the blast, as it should be, this is very ineffective.

(To be continued).

THE DETERMINATION OF SMALL QUANTITIES OF ALCOHOL.†

By FRANCIS G. BENEDICT and R. S. NORRIS.

(Concluded from p. 68).

In an experiment in which about nine-tenths grm. of 19 per cent alcohol evaporated in nine hours, no barium carbonate was formed. In two other experiments in which half that quantity of alcohol was used it was also completely absorbed by the sulphuric acid. Forty c.c. of concentrated sulphuric acid were used in each case.

Four solutions were prepared by this method, and the alcohol determined by titration. The results obtained were as follows:—

	Alcohol absorbed. M.grms.	Alcohol determined. M.grms.
I.	96·77	95·05
II.	90·87	89·66
III.	41·62	41·50
IV.	13·5	14·4

Two experiments were made to determine how much alcohol a given volume of concentrated sulphuric acid can completely remove from a current of air. In the U-tube immediately preceding the acid 90 per cent alcohol was placed, and its evaporation was facilitated by a loose roll of filter-paper in the limb of the tube next to the acid. Air was drawn through this apparatus for fifteen hours at the usual rate before a distinct appearance of barium carbonate precipitate occurred. The coating of the carbonate on the sides of the barium hydroxide tube was, at the end of this period, less in amount than that produced by the combustion of a milligrm. of alcohol. During the period approximately 40 c.c. of alcohol was evaporated. The sulphuric acid solution measured about 90 c.c., and had a brownish red colour and a faint pleasant ethereal odour. It was made up to 100 c.c. with concentrated sulphuric acid, and five-tenths c.c. measured out and made up to 50 c.c. with more acid. This solution was titrated with the chromic acid solution and found to contain 3·43 m.grms. of alcohol in each c.c. Accordingly the 50 c.c. of concentrated sulphuric acid used in the first experiment had absorbed 34·3 grms. of alcohol.

In the second experiment only 30 c.c. of sulphuric acid were used, and the alcohol was made to evaporate more rapidly. About 20 c.c. of 90 per cent alcohol were volatilised in eight hours. In the beginning of the experiment the rapid absorption of the alcohol by the sulphuric acid caused an appreciable rise in the temperature. The sulphuric acid solution was diluted as in the first experiment, and the alcohol determined to be 1·72 m.grms. in each c.c. The 30 c.c. of sulphuric acid had therefore absorbed 17·2 grms. of alcohol.

For the determinations of alcohol in dilute solutions we have found the following method the most satisfactory. Having prepared the standard solutions above described and determined the value of each in terms of the others, the strength of the unknown solution of alcohol is first determined roughly by means of an ordinary pycnometer.

If the solution contains more than 1 per cent of alcohol, weigh out accurately such a quantity as will contain about one-tenth grm. of absolute alcohol into a 50 c.c. graduated flask, add 10 c.c. concentrated sulphuric acid carefully, the flask being immersed in cold water and continuously shaken to prevent a rise in temperature. The solution is then made up to the 50 c.c. mark with concentrated sulphuric acid, thoroughly mixed, transferred to a burette, and about 5 c.c. drawn off into a small flask. Twenty c.c. of the chromic acid solution are then added, using the same precautions for the delivery of the solution as when it was standardised. The contents of the flask are heated to 98° C. (a thermometer being immersed in the liquid) and kept at this temperature for five minutes. The solution is then cooled down to the room temperature, poured into 200 c.c. of distilled water, and ferrous ammonium sulphate added from a burette until the excess of chromic acid is completely reduced, as is indicated by the disappearance of the red colour. The excess of ferrous ammonium sulphate is then determined with the standard potassium permanganate. It is best to add a single drop of the potassium permanganate solution at first in order to be sure that there is an excess of ferrous ammonium sulphate present. The amount of alcohol per c.c. is calculated thus:—The amount of ferrous ammonium sulphate solution used (after making allowance for the permanganate required for the back titration) is subtracted from the number of c.c. of ferrous ammonium sulphate equivalent to the chromic acid solution used, and the result divided by the number of c.c. of the alcohol solution taken. This gives the volume of ferrous ammonium sulphate solution in c.c. equivalent in reducing power to 1 c.c. of the solution of alcohol. Multiplying this by the factor previously determined, which expresses the number of m.grms. of alcohol equivalent to one c.c. of ferrous ammonium sulphate, gives the weight of alcohol in 1 c.c. of the sulphuric acid solution.

If the original solution contains 1 per cent or less of alcohol, draw 0·5 c.c. into a 100 c.c. flask, and add about 5 c.c. of concentrated sulphuric acid, keeping the liquid cool during the addition. Add 10 c.c. of the chromic acid solution and proceed as above. This determination will serve to indicate approximately how much alcohol there is in the solution, so that in subsequent titrations enough of it can be taken to reduce from 60 to 80 per cent of the chromic acid. The amount of sulphuric acid added in each case should be equal to about twice the volume of the solution of alcohol used.

OBITUARY.

Mr. J. A. R. NEWLANDS, F.C.S., F.I.C.

It is with much regret that we record the death of Mr. J. A. R. Newlands, who passed away on the 29th of July, at his residence at Lower Clapton, N.E., aged 60.

Mr. Newlands was best known among scientific chemists as being the first to point out the periodic relations between the atomic weight of the elements, for

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* G. Rose speaks of such loss when volatilising sulphuric acid in presence of phosphoric acid. "Handb. f. Quant. Anal.," Finkener edition, vol., ii., p. 575, and elsewhere.

† From the *Journal of the American Chemical Society*, xx., No 4.

which perhaps too much credit has been given to M. Mendeleeff. This new law, provisionally called the "Law of Octaves," was first mooted in the Chemical News in vol. vii., p. 70, February 7, 1863. In another paper in July, 1864, a list of all the known elements was given both in order of their atomic weights and in a table giving a horizontal arrangement of the more important elements, also in order of atomic weight, with blanks corresponding to some of the missing members of the various groups. Thus, in the trivalent group, commencing with boron, there was a blank next below zinc, since filled by gallium, and another below cadmium now filled by indium. On August, 20th 1864, Mr. Newlands announced the existence of a simple relation between the elements when thus arranged, to the effect that the eighth element, starting from any given one, was a sort of repetition of the first. Some years afterwards the brilliant work of Sir H. Roscoe showed the atomic weight of vanadium was 51·2 instead of 137. This reduction at once placed vanadium in the same line as the phosphorus group, thereby confirming the periodic law. Mr. Newlands leaves a large circle of friends, by whom his genial companionship will assuredly be missed. In the year 1887 Mr. Newlands was awarded the Davy Medal of the Royal Society, in recognition of his work on the Periodic Law of Elements.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

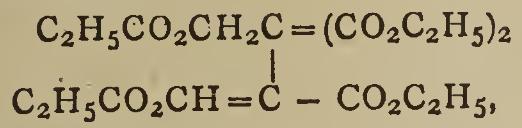
Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxx., January 24, 1898.

Gravimetric and Volumetric Estimation of Hydroxylamines and of Hydrazine.—K. A. Hofmann and F. Kuspert.—The authors estimate hydroxylamine and hydrazine by oxidising them by means of a dilute solution of sulphate of vanadyl, measuring the nitrogen give off, and titrating the sulphate of vanadium formed by $KMnO_4$.

$$2NH_2OH + O = N_2 + 3H_2O,$$
$$N_2H_4 + 2O = N_2 + 2H_2O.$$

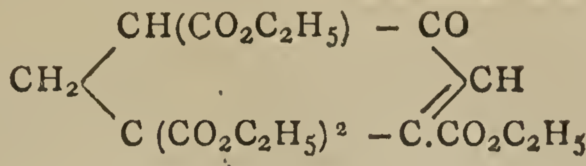
The whole of the nitrogen is set free at 60° in a few minutes. The solution of the vanadyl salt is obtained by dissolving the metavanadate of ammonium, $VdO_3.NH_4$. in concentrated sulphuric acid, and then diluting. The material to be analysed is dissolved in dilute sulphuric acid, and the vanadic solution added until it takes a green colouration; it is then heated to 60°, the nitrogen measured, &c. The end of the titration is shown by the appearance of a pale yellowish-rose tint.

Some Syntheses effected with Chlorofumaric Ether.—W. Beckh.—By treating a solution of ethenyltricarbonic ether in absolute alcohol by C_2H_5ONa and chlorofumaric ether, we obtain principally butylene-pentacarbonic ether—



$$\begin{array}{l} C_2H_5CO_2CH_2C=(CO_2C_2H_5)_2 \\ \qquad\qquad\qquad\;\; | \\ C_2H_5CO_2CH=C - CO_2C_2H_5, \end{array}$$

in the form of a viscous liquid insoluble in acids, alkalies, and water; it boils at 229—231° (13 m.m.). By saponifying this ether by $Ba(OH)_2$, we obtain butylene-tetracarbonic acid, fusing at 175—176°, easily soluble in water. The salts of silver and lead give white precipitates. At the same time as the formation of the ether, oily products are formed, giving a red colouration with $FeCl_3$; they will not distil without decomposition. Amylenepentacarbonic ether has been prepared by acting with chlorofumaric ether on carboxyglutarate of ethyl in the presence of C_2H_5ONa. It is a yellow liquid, boiling at 240—250° (15 m.m.), condensing under the influence of C_2H_5ONa at 120°, giving a cyclic compound—



which is coloured indigo-blue with $FeCl_3$.

Methylation of Hydrate of Hydrazine.—C. Harries and T. Haga.—By treating hydrate of hydrazine with increasing quantities of CH_3I we obtain successively methyl-hydrazine, dissymmetric dimethyl- and trimethyl-hydrazine. The iodhydrate, $NH_2NH(CH_3)_2I$, crystallises in water in flakes; it is fusible at 235° with decomposition, and soluble in ethylic and amylic alcohols. The chlorhydrate is hygroscopic. The oxalate of dissymmetric dimethyl-hydrazine, $(CH_3)_2N.NH_2(CO_2H)_2$, crystallises in alcohol in plates, fusible at 143° and insoluble in ether. By treating methyl-hydrazine (3 molecules) by 2 molecules of benzoic aldehyd in aqueous solution, we obtain tribenzylidene-methylhydrazine in the form of white needles, fusible at 109°, soluble in alcohol and ether, but insoluble in water.

Splitting-up of Sylvane into Levulic Aldehyd (Pentanone 3 to 1·1); Researches on the Constituents of Beech Tar.—C. Harries.—Sylvane (α methylfurfurane) is contained in considerable proportions in beech tar, in the portion boiling between 60° and 70°. This portion is exhausted by bisulphite at 40 per cent, and then by NaHO at 10 per cent. The residue dried over K_2CO_3 gives a liquid boiling at 60° to 70°. This is heated with sodium on the water-bath until there is no further reaction, and on fractionating almost pure sylvane is obtained, boiling at 65° with a density at 18° of 0·827. When heated at 120° with dilute hydrochloric acid, we obtain levulic aldehyd and its products of condensation. Methylal is easily obtained by heating 500 grms. of sylvane dissolved in 1500 c.c. of methylic alcohol, with 20 parts of methylic alcohol containing 80 per cent of hydrochloric acid gas, for twenty-four hours in a flask fitted with a vertical condenser. After precipitating with water it is dried and fractionated *in vacuo*. Methylal boils at 87—88° (17 m.m.), and has a density of 0·9684 at 18°. It is slightly soluble in water, and easily so in organic solvents. Acetal is obtained in an analogous manner, and boils at 93° (12 m.m.); it is a colourless liquid, with an agreeable odour, and slightly soluble in water. By heating methylal for ten minutes with dilute hydrochloric acid, and then neutralising with $NaHCO_3$, and then with K_2CO_3 in the presence of ether, we obtain levulic aldehyd in the form of a liquid boiling at 70° (12 m.m.), and at 108° at the normal pressure, having a density of 1·0156 at 16°. It is soluble in all proportions in water and in the organic solvents. It is stable when pure, but under the action of acids and alkalies it polymerises with great ease. Moist Ag_2O transforms it rapidly when warmed into levulic acid.

Recent Progress in Lighting by means of Flame.—H. Bunte.—The author shows that oxide of cerium is the only luminous excitant in the Auer mantle; its *role* is explained as follows:—The cerium, equally disseminated over a skeleton of thorina, provokes the rapid combination of H_2+O (as does platinum sponge), and being the only material to profit by the heat given off by the reaction, on account of the bad conductivity and the low specific heat of the thorina, the ceric oxide is carried to a temperature sufficiently high to make it strongly luminous.

Justus Liebig's Annalen der Chemie,
Vol. ccxcvii., Nov. 23, 1897.

Research on the Substituted Succinic Acids.—K. Auwers.—In this note the author gives a *résumé* of the results he has obtained with different collaborators. Of the twenty-four possible acids, $C_7H_{12}O_4$ still wants those of the *tertiary malonic butyl*, and the two stereo-isomers *αβ-dimethylglutaric.* He thinks that the αβ-dimethylglutaric acid recently described by Montemartin is only a mixture of the two stereo-isomers. The fact that symmetric di-isopropylsuccinic acid has only one modification is perhaps due to the accumulation of the groups CH_3, and not to the complication of the molecule.

Symmetric Methylethylsuccinic Acids.—K. Auwers and R. Fritzweiler.—These acids were prepared by the action of a bromobutyric ether on the soda methylmalonate of ethyl at 160°—180°. The ether of the tricarbonated acid thus obtained distils at 158°—161° (16 m.m.), and after saponification with sulphuric ether the two symmetric methylethylsuccinic acids which are separated by crystallisation; fumaroidic acid first crystallises, but in long needles, while the mother-liquor contains principally malenoidic acid, which is more fusible than the glutaric derivatives. The author then describes the preparation and properties of a large number of derivatives.

On Asymmetric Methylethylsuccinic Acid. — K. Auwers and R. Fritzweiler.—This acid was obtained by the action of malonic soda ether on methylethylacetic ether. To prepare this latter the authors first prepared ethylmalonic ether; then ethylmethylmalonic ether, by the successive ethylation and methylation of malonic ether, and then saponifying the ether and heating the ethylmethylmalonic acid to get rid of the CO_2. The ethylmethylacetic acid was then bromised and etherified. The action of malonic soda ether on this body, to obtain the tricarbonated ether, gives but a poor return (29 per cent). The methylethylsuccinic acid passes over at 145°—155° (30 m.m.), and the glutaric derivative at 190°—210° (30 m.m.).

The Isopropylsuccinic Acid Derivatives of Amylene. — K. Auwers and F. Meyer. — The amylene boiling at 29°—35° was converted into dicyanide, and the acid resulting from the saponification of this nitrite was recognised as *isopropylsuccinic acid.*

The Symmetric Bidecylsuccinic Acids.—K. Auwers and F. Betteridge.—Lauric acid, $C_{10}H_{21}.CH_2.CO_2H$, was bromised and then etherified. The α-bromolaurate of ethyl distils at 170°—174° (11 m.m.). From this bromised ether bidecylsuccinic ether is prepared, distilling at 200°—205° (12 m.m.).

On δ-Methyluric Acid.—W. von Lœben.—Not suitable for abstraction.

On Phenacetylmalonic Ether.—H. Metzner.—This ether, prepared by chloride of phenylacetyl and malonic soda ether, gives benzylmethylacetone,—

$$C_6H_5.CH_2—CO.CH_3,$$

when warmed with HCl. Soda splits it up into malonic ether and phenyl-acetic acid. An analogous splitting-up is produced by concentrated NH_3, which gives malonic and phenacetic amides.

MISCELLANEOUS.

Sulphate of Ammonia Committee Prize Essay.—We may draw attention to the offer by the Sulphate of Ammonia Committee of the sum of 500 guineas for the best essay on "The Utility of Sulphate of Ammonia in Agriculture." The subject is to be treated from a practical and scientific point of view. The committee, we are told, has secured the services of Mr. William C. Little and Dr. Voelcker to act as judges of the essays, and in the event of any difference arising, Mr. Samuel Rowlandson will act as referee. The essays must be in the English language, and be in the hands of the Chairman of the Committee not later than November 15. The selected essay will become the property of the committee, who reserve to themselves the right to make such use of it as they may think fit. The committee also reserves to itself the right to purchase for a sum not exceeding 50 guineas any of the other essays. Further particulars can be obtained of Mr. W. G. Blagden, Chairman of the Sulphate of Ammonia Committee, 4, Fenchurch Avenue, London, E.C., to whom we would refer intending competitors.

The Chemical Laboratory at Wiesbaden.—During the Summer Term, 1898, the Laboratory was attended by 38 students. These may be divided, according to their respective countries, as follows: — From the German Empire there were 26; from Austria, 3; from England and from Brazil, 2; from Luxemburg, Russia, and Bulgaria, 1 each. There were 3 Assistants in the Instruction Laboratory, and 23 in the Versuchsstationen (private laboratories). In the certified body of Teachers there has been no change: to this body belong the Directors, Professor Dr. H. Fresenius, Professor Dr. W. Fresenius, Professor Dr. E. Hintz, and also Dr. med. G. Frank, Dr. W. Leng, Dr. L. Grünhut, and T. Brahm (architect). On the 25th and 26th May, 1898, the Laboratory was able to celebrate the event of its fifty years' existence. The continuation of support from the State has been guaranteed to the Institution, together with the right of the practical instruction of provision and food analysts for the final examination. The Winter Term begins on October 17th. Besides scientific work, numerous researches have been made during the past Summer Term in the interest of commerce, industry, mining, agriculture, sanitation, law, and the administration, in the Versuchsstationen (private laboratory).

Methyluric Acid and Dimethyluric-1.7-Acid. — E. Fischer and H. Clemm.—Methyluric acid is easily prepared from theobromine, which is oxidised by HCl and $KClO_3$ and precipitated with SH_2; this gives dimethylalloxantine, which is treated with HNO_3 and transformed into methylalloxane. One part of methylalloxane is heated with 12 parts of a concentrated solution of sulphide of ammonium at 80° for six hours. After cooling, the precipitate is transformed into methyluranile by HCl gas. This body is warmed with one part of CNOK and three parts of water until the red colour disappears. On cooling, methylpseudourate of potassium crystallises out; this is decomposed with HCl. The methyl-pseudo-uric acid is transformed into methyluric acid by heating with 9 parts of HCl at 20 per cent for one hour on the water-bath. Methyluric acid, $C_6H_6N_4O_3$, crystallises in needles decomposing without melting at 400°. Dimethyluric acid-1.7 is prepared by heating three parts of methylalloxane with five parts of methylamine at 33 per cent, previously saturated with SO_2. The cooled solution is treated with excess of HCl. The dimethylpseudo-uric acid obtained is heated with KCl at 20 per cent, which gives dimethyluric acid-1.7.—*Ber. Deutsch. Chem. Gesell.*

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ON BLUE GLASSES WITH A BASE OF CHROMIUM.

By ANDRE DUBOIN,
Professeur adjoint à la Faculté des Sciences de Clermont-Ferrand.

The experiments through which sapphire has been reproduced have led people to think that the fine blue colour of that gem is due to chromium. Ste.-Claire Deville and Caron (*Comptes Rendus*, 1858, xlvi., p. 764), after their experiments on the reproduction of corundum, in the course of which they obtained both sapphire and ruby, are quite positive on this point. "Blue sapphire," they say, "is produced under the same circumstances as ruby. It is likewise coloured by oxide of chromium. The only difference between them lies in the proportions of the colouring matter, perhaps also in the state of oxidation of the chromium. But analysis can give no accurate results on this point, owing to the very small quantity of colouring matter present in all cases. In certain preparations people have obtained, side by side, red rubies and sapphires of the finest blue, whose tint is, moreover, exactly the same as that of the Oriental sapphire, the cause of which is unknown."

Later on, Gaudin (*Comptes Rendus*, 1869, xlix., p. 1343) observed that the oxide of chromium, heated in the reducing flame of the oxyhydrogen blowpipe, takes a sky-blue tint, though somewhat greenish. This tint is to be found in some Ceylon sapphires.

The blue tint of sapphire is due to chromium, so it must be possible to obtain, with the help of the compounds of chromium, blue glasses by operating in a reducing medium.

I at first ascertained that, by heating some alumina along with a small quantity of oxide of chromium, a pink colour is always obtained; but I have obtained no blue colour by heating it along with a reducer (charcoal, aluminium, &c.).

In such cases oxide of chromium was entirely reduced. Oxide of chromium, highly heated with aluminium in small particles, is reduced with explosion.

Then I operated with B_2O_3 and SiO_2 with a view to obtaining glasses.

At first I tried the hard glasses, with a base of alumina, used in the making of artificial gems.

It is known that with this object fusible mixtures are used, the composition of which comes very near the formula $4{\cdot}5SiO_2,Al_2O_3,3CaO$. Part of the lime may be replaced by an equivalent quantity of baryta to obtain glasses having more brilliancy, and whose density comes nearer to that of precious stones.

With a view to colouring these glasses by means of the oxide of chromium I proceeded as follows:—I heated to vivid redness for five hours, in a crucible brasqued with charcoal, the vitrifiable mixtures with some neutral chromate of potash. I have, moreover, ascertained that this salt may be replaced by an equivalent quantity of $Cr_2O_7K_4$ or Cr_2O_3.

1. A mixture of SiO_2 (135 parts), Al_2O_3 (51), CO_3Ca (150), CrO_4K_2 (9), to which some arseniate of potash has been added, gives a crystalline mass which I mean to study at greater length, but which, from our present point of view, has only a somewhat dull blue tint.

2. On the contrary, compounds which contain baryta give most beautiful blue glasses. I replaced the whole quantity of lime by the equivalent quantity of baryta. The vitrifiable mixture used is made up of SiO_2 (135 parts), Al_2O_3 (51), CO_3Ba (295·5), CrO_4K_2 (7). It gives when melted a very fine blue glass.

I was then led to seek whether I could not obtain a composition still more fusible and equally bright. It is known that a mixture of CO_3K_2 and CO_3Na_2, or KCl and NaCl, or K and Na, melts at a lower temperature than each of the bodies taken separately.

I therefore tried to replace half the lime by the equivalent quantity of baryta; the mixture used being composed as follows:—SiO_2 (135 parts), Al_2O_3 (51), CO_3Ba (148), CO_3Ca (75), CrO_4K_2 (9). It gives, when melted, a very fine blue glass.

3. *Glasses with Boric Acid.*—It is known that in glasses a part of the SiO_2 may be replaced by boric acid. I obtained a glass of a very fine blue tint, but too easily attacked by acids, by melting under the same conditions as before a mixture of B_2O_3 (4 parts), Al_2O_3 (1 part), CrO_4K_2 (1 part). In this experiment a glass is obtained which is surrounded with a pellicle of metallic chromium. Very often the crucibles are pierced. If borax is substituted for boric acid, the alumina is reduced. In an experiment in which I had heated a mixture of borax and alumina with a small quantity of CrO_4K_2 and a quantity of SiO_2 equal to two-fifths of the alumina, a metallic pellicle was formed, consisting for the most part of aluminium.

I made numerous experiments until I found the composition of a glass made by Messrs. Schott and Co. at Jena. I have been able to colour this glass blue by means of the oxide of chromium. The mixture used was composed as follows:—SiO_2 (84 parts), Bo_2O_3 (39), Al_2O_3 (16), CO_3Ba (157·6), CrO_4K_2 (7).

In the course of my numerous experiments on this subject, I tried various reducers; among others, Al and carbide of calcium. Aluminium did not lead to good results; but, by operating at a higher temperature, it might be possible to obtain results more satisfactory than those I obtained. As for C_2Ca, it gave me blue glasses, not so fine, however, as the above-mentioned. In the latter case I operated in a graphite crucible. Practically, there would be some difficulty in regulating the quantity of C_2Ca to be used, as the material employed is always somewhat hygroscopic.

4. *Common Glasses.*—Common glasses, or the mixtures used in obtaining them by melting, did not give good results. A mixture of 100 parts of quartz, 30 of CO_3K_2, 15 of CO_3Ca—a composition answering to that of Bohemian glass—to which 7 parts of CrO_4K_2 are added, gives a glass which has a bluish violet hue only in the vicinity of the layer of carbon. Better results might perhaps be obtained by heating during a longer time. As for glass itself, pulverised and melted with CrO_4K_2, it gave me only a green glass.

ON THE
ANALYSIS OF CRUDE TARTROUS MATERIAL.

By M. J. SCHAFER.

Among the many methods for the estimation of tartaric acid in tartrous substances, the one most used is that of Goldenberg—a process which is based on the setting free of the tartaric acid by means of hydrochloric. The free acid is transformed into a neutral potassic salt by means of carbonate of potassium. The liquid is evaporated down to a small volume (10 c.c.), and glacial acetic acid is added; this causes the partial precipitation of the tartar. To make the precipitation complete we add a known volume of alcohol at 96 per cent, allow to stand for a certain time, then filter. The precipitate is washed, dissolved in warm water, and the solution thus obtained titrated while still warm with normal soda.

Such is, in brief, the original process which has been adopted in most laboratories. However, with this process a larger proportion of tartaric acid is found than is really present in the substance examined, and this error—though relatively small—is considerably augmented if the original method is not closely followed. It is in this manner that Möslinger introduced certain modifications giving wide variations. For observing the progress of the titration this author used azolithmine with a violet shade instead of red litmus-paper; he left the precipitate formed by the glacial acetic acid for a whole night in the aceto-alcoholic liquor, while by Goldenberg's method only a short time of standing is recommended; to precipitate the tartar he used 5 c.c. of glacial acetic acid, while the original process only speaks of 2 to 2·5 c.c.

By using blue azolithmine paper the titration is continued until a drop of the liquid placed on the paper no longer produces a red colouration, while in the original process it is stopped when a drop gives a slight blue colour to red litmus-paper. In the case of mineral acids there is no difference between these two indicators, but it is altogether different with tartaric acid; in this case the change from red to blue is retarded. This applies even to chemically pure tartar. But when we have to deal with crude tartars or wine lees, still other factors intervene and increase the difficulties of the titration. The precipitate caused by the glacial acetic acid contains, besides the tartar and chloride of potassium, other bodies which neutralise a certain quantity of the alkaline solution, and thus cause a doubtful reaction. It is for this reason that it often happens that the red litmus-paper becomes decidedly blue, while the azolithmine paper is still red. The difference that these two critical points will sometimes reach is as much as 1·5 to 2 per cent, especially with poor samples.

The time during which the precipitate caused by the glacial acetic acid is left standing also has a considerable influence on the results of the analysis. I have proved that the precipitation is complete at the end of a quarter of an hour, and that by letting the solution stand too long the results obtained are too high, on account of the formation of a flocculent precipitate which saturates a certain quantity of the alkaline solution. Below we give some very interesting results:—

	Tartaric acid found after standing for—		
	¼ hour.	3 hours.	12 hours.
French lees ..	23·24	23·47	24·27
Spanish lees ..	24·93	25·17	26·16
Portuguese lees..	24·22	24·67	25·29
Unknown lees ..	15·45	15·67	16·27
Portuguese tartar	54·22	54·64	54·94
Portuguese lees..	22·80	23·00	23·50
Spanish lees ..	28·27	28·68	29·36
French lees ..	27·88	28·17	28·66
Algerian lees ..	21·87	22·57	22·87

But by exhausting the material by a mixture of ether and alcohol before analysing, the precipitate can be left for a considerable time without the results being adversely affected. Below will be found some figures on this subject:—

	Tartaric acid found—	
	Filtering immediately.	After 12 hours.
Italian lees ..	29·33	27·38
Spanish lees ..	25·27	25·37
Spanish lees ..	28·60	28·70
Algerian lees ..	22·33	22·33

These small differences are due to the inevitable errors of observation. My researches have enabled me to arrive at the following conclusions:—

1. The end of the titration should be decided by the use of pale red litmus-paper.

2. The operation is complete when a drop of the liquid placed on this paper forms a circle bordered with blue.

3. As soon as the glacial acetic acid has completed the precipitation of the tartar, the liquid should be filtered,—if not, another body is formed which saturates a certain quantity of the alkaline liquor, and thus causes too high a result. The quantity of this body formed is in direct proportion with the time the solution is left standing.

4. When the material is exhausted with a mixture of ether and alcohol, before analysis, the whole may be allowed to stand for a much longer time without inconvenience.—*Chemiker Zeitung*, 1898, p. 255.

ON ANHYDROUS AND CRYSTALLISED SULPHIDE OF MAGNESIUM.

By A. MOURLOT.

Sulphur and magnesium unite directly at about 600°, forming a sulphide with the formula MgS, which is recognised as a grey, porous, amorphous, and infusible mass. A certain number of reactions enable us to obtain this compound indirectly; in the latter case we obtain a white powder which decomposes very readily.

The research we have made on the action of a high temperature, and of reducing agents on sulphates, made it possible for us to obtain this body melted and crystallised.

I. *Preparation of the Amorphous Sulphide.*—It was necessary for the proper carrying out of these researches to be able to prepare fairly large quantities of the amorphous sulphide: for this purpose, after having tried either Fremy's method (*action of sulphide of carbon on magnesia at a red heat*), or that of Reichel or of Parkinson (*action of sulphur vapours carried by hydrogen over red-hot magnesium*), we finally adopted the two following methods:—

1. We placed a mixture of magnesium filings and a small quantity of sulphur in a carbon boat, which was placed in a porcelain tube heated in a reverberatory coke furnace; the tube was traversed by a continuous current of sulphuretted hydrogen; the reaction takes place with strong incandescence. We thus obtain rapidly the amorphous sulphite of a white colour, or with a slight greyish tinge.

2. A second process consists in making sulphuretted hydrogen react on the anhydrous sulphate, or on pure magnesia heated to about 1200°; however, the complete transformation of the magnesia into sulphide is very slow, as shown by Reichel (*J. f. Prakt. Chim.*, xii., p. 55). If we operate on 20 grms. of sulphate the transformation is complete after four or five hours' heating; abundant sulphur vapours are given off, as well as sulphurous acid gas and water.

In these two methods we use an apparatus for the continuous supply of sulphuretted hydrogen. The tube is allowed to cool in a vapour of hydrogen.

On analysing the amorphous sulphide we obtained the following results:—

	I.	II.	Theory.
Mg ..	43·05	43·15	42·85
S ..	56·85	56·80	57·15

II. *Preparation of the Melted and Crystallised Sulphide.*—1. The amorphous sulphide is placed in a carbon boat, and the latter is introduced into the carbon tube of a tubular electric furnace. After about six minutes heating by means of a current of 1000 ampères and 50 volts, we obtained a globular yellowish mass, of a brilliant appearance and well melted: this experiment was repeated a certain number of times, varying the time of heating, but we always obtained the same product.

2. We further tried to prepare the crystallised sulphide directly, in the electric furnace, by reducing the anhydrous sulphate by carbon. This method, which gave us such good results with the alkaline earthy sulphides, only gave in this case an incomplete transformation of

the sulphate into sulphide, a certain quantity of the sulphate being at the same time brought to the state of magnesic oxide.

3. We then endeavoured to utilise the phenomena of double decomposition which might take place between the chloride of magnesium and certain sulphides. For this purpose we mixed sulphide of magnesium, in slight excess, with proto-sulphide of tin, in the proportions shown by the formula $MgCl_2+SnS$, and we submitted this mixture to the action of a current of 1000 ampères and 50 volts. There was an abundant disengagement of vapours of chloride of tin, and after about seven or eight minutes the heat was stopped, and small globules of melted sulphide of magnesium were found, completely identical with that produced by the fusion of the amorphous sulphide. The analysis of the crystallised sulphide gave us:—

	I.	II.	Theory.
Mg ..	43·23	43·6	42·85
S ..	56·65	56·3	57·15

Properties.—Melted sulphide of magnesium is formed of large globules with a crystalline fracture often showing faces of cubical crystals; two distinct cleavage planes have been observed at right angles to each other; these crystals do not act upon polarised light; they are insoluble and are without action on essence of turpentine at the ordinary temperature; their density, taken in this liquid, is 1·85.

Hydrogen is without action on crystallised sulphide of magnesium at the highest temperature which can be obtained in a reverberatory furnace. Chlorine reacts at about 300°, with incandescence, producing anhydrous chloride of magnesium as well as chloride of sulphur. Bromine and iodine react at a dull red heat with the formation of the corresponding bromides and iodides, but without incandescence.

The action of oxygen is also very vigorous, and takes place with a slight elevation of temperature, though without any disengagement of sulphurous acid gas. The energetic oxidising agents, chlorate of potassium, binoxide of lead, and nitrate of potash, all react with incandescence.

With phosphoric anhydride there is further the production of a sulphide of phosphorus.

Phosphorus does not react on crystallised sulphide of magnesium; the experiment was tried in a current of carbonic acid gas, and there was no trace of any reduction even at 1000°. Boron and silicon, heated with the sulphide in a current of hydrogen, do not react up to a red-heat. The action of carbon was tried in the electric furnace; after heating for about fifteen minutes with a current of 1000 ampères and 50 volts, no reduction took place.

Iron is without action at a dull red-heat; sodium, on the contrary, does react, but without incandescence.

Aqueous vapour reacts directly with the production of magnesia and the disengagement of sulphuretted hydrogen; at the ordinary temperature the crystallised sulphide is very difficultly attacked by water, though in the case of the amorphous sulphide the decomposition is immediate. Concentrated nitric acid attacks it in the cold with the formation of sulphur; sulphuric acid, even when diluted, reacts at the ordinary temperature with the disengagement of sulphuretted hydrogen.

Gaseous hydrofluoric acid as well as hydrochloric acid gas react in the cold; by slightly heating, incandescence takes place with the production of the anhydrous fluoride or chloride. The reaction with hydrobromic and hydriodic acids take place at a dull red-heat with the formation of the bromide or iodide; but in this case there is never any incandescence.

The metallic chlorides react on crystallised sulphide of magnesium, under the influence of a slight rise of temperature; with the trichloride of phosphorus the reaction takes place with a considerable disengagement of heat and the formation of sulphide of phosphorus.

With subchloride of chromium the reaction is also very vigorous; in this latter case a greenish body containing chromium and sulphur is produced. We shall follow up the study of this body.

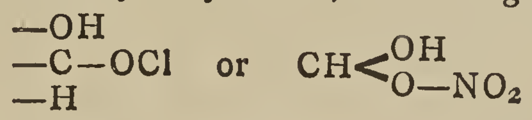
To sum up:—1. We have described an easy method for the preparation of anhydrous sulphide of magnesium. 2. We have prepared crystallised sulphide of magnesium both by the fusion of the amorphous sulphide and by the action of chloride of tin on anhydrous chloride of magnesium. 3. From the study of the properties of crystallised sulphide of magnesium we find that this sulphide is much less easily decomposed than the amorphous sulphide, and that it resembles sulphide of barium in most of its reactions. It is particularly remarkable for its complete irreducibility by carbon, which ranges it with the sulphides stable at a high temperature.—*Comptes Rendus*, cxxvii., No. 3.

THE

INVERSION OF SACCHAROSE BY WATER.

By MM. RAYMAN and SULE.

The mechanism of the inversion of saccharose has up to the present remained very obscure. The acids capable of producing the inversion have not the property of forming any combination with either of the two sugars resulting from the hydrolysis of the molecule; and, admitting that such compounds are formed, they should be very unstable and instantly destroyed by water; in fact a grouping—



$$\begin{matrix}-OH\\ -C-OCl\\ -H\end{matrix} \quad \text{or} \quad CH{<}^{OH}_{O-NO_2}$$

would be very easily attacked by water. In the case of organic acids, we could easily imagine the production of relatively stable acid-aldehyds, but this hypothesis cannot be correct, as a very small quantity of acid suffices to hydrolyse a large quantity of sugar. On the other hand, we are well aware that the inversion by water only is possible above 110°. When we mix an acid with the water, the minimal temperature of inversion is lowered in proportion as the acid is energetic, and the inversion by water in the presence of acids may be considered as a generalisation of the laws established by Landolt and Ostwald.

There is already abundant but contradictory literature on the subject of inversion by water. Monier and Trevor found that a neutral aqueous solution could be kept at a temperature of 100° to 105° for two hours and a half without undergoing decomposition. Soubeyran gives polarisations of such an irregular character that they really cannot be believed.

In our experiments we took very great care to use only the very purest saccharose, and water completely free from any foreign matter. The water was distilled in a Bohemian glass retort after permanganate of potash had been added to it, and the distillate was again distilled with alum. Its electric conductivity, after this treatment was 1×10^{6}.

To prepare the saccharose we dissolved 250 grms. of the refined material, as pure as we could obtain it, in 150 grms. of warm water; the syrup was filtered through cotton-wool, and after cooling was poured in a very fine stream into one litre of alcohol at 96 per cent while constantly agitating. The following day there was a crust of crystals of saccharose on the surface. The mother-liquor was decanted, the crust washed with alcohol, and a fresh solution of 250 grms. of sugar in 150 grms. of water was added. This treatment was repeated three times; these crystalline crusts were coarsely powdered, washed first in alcohol, then in ether, and dried in vacuo at 40°—45°.

The rotatory power of the sugar thus obtained is $\alpha_D = +66{\cdot}55$.

Decomposition of Saccharose by Water in Glass Vessels.—We made a number of solutions of different concentrations in both Bohemian and Jena glass vessels; these were boiled and the glasses weighed both before and afterwards. Solution No. IV. was heated on a water-bath; the polarisations obtained in a tube 10 centimetres long were :—

Time.	I.	II.	III.	IV.
0 hour	3·22	6·01	11·66	11·66
6 hours	3·24	6·10	11·66	11·67
67 „	3·24	5·96	11·57	11·64
33·5 „	3·24	—	10·56	10·97
61 „	3·14	—	5·94	6·82

Thus the inversion is the more complete as the solution is the more concentrated; the boiling-point is only 0·8° higher than that of water. The results are not varied by passing a current of oxygen through the boiling solution, and the solutions remain perfectly neutral.

We may therefore admit that even a prolonged boiling will not invert weak solutions.

The presence of the smallest quantity of salts, indicated by an increase of conductivity, increases the inversion. Thus a 20 per cent solution of saccharose made with a water whose conductivity was 20×10^6 gave as polarisation :—

Hours . ..	0	4	8	12	16	20	24
Polarisation	11·8°	11·67°	11·34°	9·74°	5·26°	0·23°	2·53°

Decomposition by Water in Platinum Vessels.—We used a platinum flask with a condenser of the same metal. After having kept up the boiling for the required time we cooled down, brought to the original volume and polarised; the reaction remained perfectly neutral, and we noticed that the inversion became very energetic after the sixteenth hour:—

Hours—	0	4	8·5	10·5	14	16	18	21·5	25
Polarisation—	13·25°	11·75°	11·28°	9·11°	4·41°	0·86°	−1·97°	−3·27°	−3·42°

Metal Receivers.—As we have just seen, the inversion is rapid in platinum, even with a very pure water, of which the conductivity did not exceed 1×10^6. In another experiment, after 20 hours and a half we reached a final polarisation of −4·13, while by calculation a total inversion would have been 4·17. However, it is impossible to get theoretical figures on account of the destruction of the fructose which takes place.

To eliminate the action of the air, the experiment was repeated in platinum, but the solution of sugar was covered by a layer of pseudo-cumol. We found that from 11·73 the polarisation altered to — 2·88 after 15 hours, but that the solution became acid. This showed us that the inversion might be due to two causes, either the contact with platinum or on account of the acid formed by the auto-oxidation of the sugar. As to the nature of the metal, it does exercise an influence. We made a series of experiments with vessels of copper, silver, and platinum :—

Time.	Copper.	Silver.	Platinum.
0 hours	11·57°	11·57°	13·25°
4 „	11·45	11·56	12·75
8 „	10·72	11·0	11·60
12 „	7·17	8·98	7·45
16 „	0·47	4·40	0·86
18 „	1·93	−1·44	−1·97
23·5 „	—	−2·95	−3·39
31 „	—	−3·59	—

The Influence of Pulverulent Metals.—The experiments made with platinum showed that the platinum metals in a state of fine subdivision should have a very energetic reaction. In a series of flasks of hard glass we placed 50 grms. of a solution of sugar and 1 grm. of metal, and heated on a salt-water bath. Comparative trials were made on the same water-bath, but without the addition of any metal. The following results were obtained :—

Time.	Solution alone.	Palladium.	Platinum sponge.	Rhodium.
0	11·90	11·90	11·90	11·90
4	11·53	−3·45	10·88	9·37
9	9·0	—	4·0	−1·32
12	5·92	—	0·74	−3·04
15	2·32	—	−1·67	−3·72

In these experiments the inversion was more rapid because the water used had a greater conductivity.

The action of palladium is the most interesting, because it was very energetic, and the palladium was able to absorb the gas produced. In a certain number of cases the solution became acid, and formic acid was detected. By forming silver salts of the acids thus obtained and carrying the temperatures to boiling point, carbonic acid was given off; and an odour similar to that of valerianic acid was noticed. Finally, traces of a non-volatile acid were found, but we were not able to identify it.

The study of the electric conductivity of the solution shows that the addition of palladium causes a great diminution of the resistance, and that the reaction goes on, but with less and less energy as time advances.

Temperature also has a great influence on inversion. At 40° and even 60° no inversion takes place, even in the presence of platinum; in fact, the inversion is always weak during the first few hours.

It appears from these experiments that the inversion of sugar by water only in the presence of metals gives a double phenomenon, the hydrolysis of the sugar and the formation of acids at the expense of the molecule of saccharose.

The Influence of Pressure.—Preliminary trials have shown that the inversion of saccharose under great pressure was far less marked than at the atmospheric pressure, and according to special experiments made by the authors on etherification, the latter showed similar results. There would thus appear to be an analogy between the inversion of saccharose by water and the formation of alcoholic ethers.—*Zeits. fur Zuck. Ind. in Bohem.*, p. 234, 1898.

THE
EXISTENCE AND DIFFUSION OF GLUCOSE.

By M. BEIJERINCK.

Beijerinck describes, under the name of amylases, the enzyms which break up starch; the granulases are amylases which transform starch into maltose and achroodextrine. It is admitted that amylases are easily diffusible bodies. Beijerinck made use of the diffusion of an aqueous solution of amylase in starch and gelatin for the purpose of studying three phenomena of the hydrolysis of starch. The following three methods were used :—

1. Diffusion in solid media to separate the enzyms.
2. The reaction of iodine, to show the formation of achroo- or erythro-dextrine.
3. The development of bacteria in solid media, to prove the presence of sugar as glucose and maltose.

Method of Diffusion.—A 10 per cent aqueous solution of gelatin is prepared, to which ½ per cent of fecula—or, better still, soluble starch—is added. The whole is boiled for a few moments, and then run in very thin layers into well-polished glass dishes; the grain of barley to be examined is cut with a razor down its axis, and the newly cut surface is applied to the gelatin-starch. The two enzyms, maltase and granulase, become diffused, and the limit of the field of diffusion can easily be seen with the naked eye; the place is then left alone for two days in an atmosphere of chloroform, to prevent the growth of moulds, after which iodised iodine is poured over the plate. The field of diffusion appears colourless, surrounded by a reddish-violet ring which separates it from the unattacked parts which are coloured blue. Maltase diffuses quicker than granulase, which will explain the existence of the violet ring, due to the presence of erythro-dextrine; in fact, the maltase changes the starch into a mixture of maltose and erythro-dextrine. In the interior of the ring the granulase has changed the erythro-dextrine into malto-dextrine not coloured by iodine, and finally into maltose.

The violet ring is very narrow when we use germinated barley, and, on the contrary, it is very wide when we use non-germinated grains: this shows that granulase does not exist before germination and develops at the same time as the embryon.

Maltose diffuses quickly all over the plate, and cannot be made visible by the auxanographic method.

Glucase transforms maltase into glucase. The latter can be detected on the plate by means of levures which cause the glucose to ferment, but not the maltose; it suffices to mix the cells of these levures with the gelatin, and the colonies formed indicate the presence of glucose.

Auxanogramme.—We prepared a solution of gelatin containing:—

10 per cent of gelatin.
0·5 grm. of acid phosphate of potash.
5 grms. of maltose, dextrine, or ½ per cent of soluble starch.
0·25 grm. of asparagin or 1 per cent of peptone.

If this solution is mixed with a culture of *Sacch. apiculatus*, *fragrans*, or *kefyr*, and then left in a flat glass dish, and afterwards treated with a solution of glucase, a development of levure takes place at the points which are attacked by the glucase: this development is indicated by a well-marked cloudiness forming the auxanogramme of the levure.

If soluble starch has been used, we only find colonies in the immediate neighbourhood of the particles of glucase, on account of these being but very slowly diffused, which is contrary to what happens in the case of the diastase of malt; soluble starch also diffuses very badly. When maltose is used the result is much more easily seen, the sugar diffusing without difficulty.

We also recommend the use of the mycoderm, which developes easily and quickly; it, however, has the inconvenient property of also attacking maltose in the presence of malt peptone, while this action does not take place if we use ordinary peptone, asparagin, or ammoniacal salts.

The glucose of the levure is destroyed at 55°; there appears to be a particular enzym in oats similar to granulase, but we cannot make quite certain that glucase is a chemical entity; on the contrary, it is very probable that there are several modifications in existence, each corresponding to some known grain, such as maize, sorgho, sarrasin, &c.

Beijerinck has studied the three principal species of amylase, according to the products they give with granulose and starch paste; he is of the opinion that, apart from maltose and glucose, three different kinds of dextrine can be obtained—erythro-dextrine, malto-dextrine, or isomaltose and leuco-dextrine; the first alone gives with iodine a violet colour, the other two have every appearance of the achroo-dextrines. Under the name of leuco-dextrine, the author means a mixture of bodies precipitated by alcohol at 60 per cent from a starch paste, at the moment when colouration by iodine ceases. With concentrated alcohol one obtains malto-dextrine in the form of a syrup. Leuco-dextrine should arise from the cellulose of the starch cell, while granulase should produce erythro-dextrine, malto-dextrine, and maltose. Leuco-dextrine contains a mixture of bodies, some easily diffusible and others exactly the opposite. Leuco-dextrine can, in a neutral or faintly alkaline medium, be converted into maltose by ptyaline or the diastase of the pancreas, while in a faintly acid solution it passes through glucase to the state of glucose.

The breakings-up occur much more slowly with this body than with granulase. The author designates under this name the portion of a solution of starch which is rapidly attacked by the diastase of malt. We can detect two groups of granulases, the acid and the alkaline. To the first group belongs ptyaline and the granulase of pancreas; to the second the granulase of the embryon of barley and wheat, also that of sarrasin, identical with the granulases of the dicoytyles, which are as a rule met with in seedling potatoes and the granulase of the maize germ, &c.

Maltases.—We meet with enzyms of this nature in wheat, barley, rye, and in the organs of a certain number of other vegetables.

Mueder estimated that there would therein be a large number of amylases. Dubrunfaut and Castinier, in 1881, showed that two separate enzyms existed in barley malt. But it is Wysman, with his theory of the two enzyms, who is the most precise. It is, however, necessary to modify his interpretation of the phenomena to some extent.

The dextrinase of Wysman would in fact be, according to Beijerinck, an artificial product resulting from the heating of the amylase of malt for ten minutes at 78°, but it does not actually exist in malt. If we heat the amylase of malt, formed by a mixture of maltase and granulase, to a temperature of 70°, the maltase, which is already weakened at 55°, is completely destroyed, while the granulase only undergoes a slight modification; it partially takes its power of forming maltase, while its faculty of creating dextrine remains intact. The property of liquefying starch paste belongs to granulase, and not to a special enzym.

The author describes his process for the preparation of glucose from maize, making use of the fractional precipitations by means of alcohol.

An interesting point is the transitory formation of dextrine by the glucase acting on the starch paste or on soluble starch; the proof of this is furnished by the auxanographic method in a most ingenious manner. A gelatin plate is prepared, to which has been added *Sacch. ellipsoideus*, but the gelatin only occupies one-half of the plate, and contains 10 per cent of gelatin, 0·5 of soluble starch, 0·25 of asparagin, and 0·005 of phosphate of potassium. The other half of the plate is covered with a similar gelatin, with the exception that it does not contain any starch; glucose is deposited on the two sides of the line separating the two kinds of gelatin. In the first half circle a development of levure is quickly noticed; a little later we also observe a semicircular auxogramme under the glucose in the second half-circle. As a matter of fact, the dextrine first formed by diffusion has spread to the second half, and has been transformed into glucose in the place where it came in contact with glucase.—*Centralblatte fur Bakteriologie*, ii., p. 221, 1897.

A COLLECTOR FOR DISTILLATION OF AMMONIA FROM WATER.

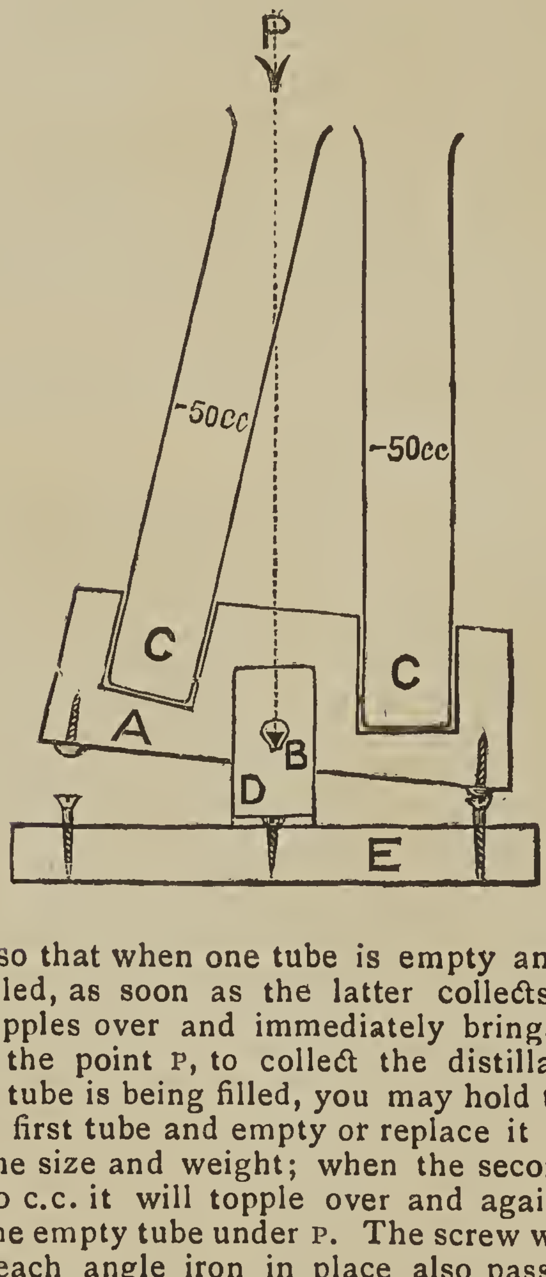
By F. P. DUNNINGTON.

In the familiar process of making a determination of free and albumenoid ammonia in water, the close attention which is demanded to change the receptacle as each of the several portions of 50 c.c. is collected, is somewhat engrossing to anyone when conducting other analytical work. To avoid this embarrassment I have devised the following simple apparatus, which, for lack of a better name, is called a collector.

The figure presents a section of one-fourth size. From this the arrangement and working of the apparatus may be understood. It is made as follows :—

In a block of dry poplar or other light wood, A, 43 × 53 × 150 m.m., a hole of 3 m.m. diameter is made at B for the pivot, and the large holes, C C, for Nessler tubes, are placed at the same distance from the centre of the block and equally inclined, as indicated. When the Nessler tubes are 29 m.m. in diameter, these holes should be about 31 m.m. and be lined with a strip of woollen cloth to afford a snug fit for the tubes. The pivot B is a knife edge, made by grinding at its ends, a piece of a double three-inch saw file about 55 m.m. long, and is merely hammered into the small hole cut for it. The knife edge is supported by a pair of plain two-inch angle irons (such as are kept in stock at a hardware store) ; in each of these, the hole in the upright limb is bored out and filed to the shape shown in the figure. These irons, D, are screwed to the wooden base, E, 170 × 170 × 20 m.m.

The motion of the block A is checked by two round-head screws fastened into the under side of A, and by two flat-head wood screws partly screwed into the block E. By screwing the latter up or down you may adjust the apparatus so that when one tube is empty and the other is being filled, as soon as the latter collects 50 c.c. of water, it topples over and immediately brings the other tube under the point P, to collect the distillate. While the second tube is being filled, you may hold the block A, remove the first tube and empty or replace it by another tube of same size and weight; when the second tube has collected 50 c.c. it will topple over and again bring the mouth of the empty tube under P. The screw which serves to fasten each angle iron in place also passes through one end of a slip of thin sheet brass 15 × 30 m.m., the other end of which is bent up at right angles, so serving to keep the pivot from shifting to one side, but not binding upon it. This piece of brass is not shown in the figure, since it would cover the pivot end.



The Nessler tubes used are 29 m.m. in diameter and 195 m.m. long, and weigh 49 grms. ; should the tubes be heavier, it would be necessary to bore the hole for the pivot at a point a little higher up on the centre line of the block A. It is easy to adjust this apparatus so that the amount required to topple the tubes will not vary as much as one-half c.c. from the 50 c.c.—*Journal of the American Chemical Society*, vol. xx., No. 4.

A REDUCTION OF PERMANGANIC ACID BY MANGANESE PEROXIDE.*

By H. N. MORSE and C. L. REESE.

(Concluded from p. 79).

The next series of experiments was designed to determine the relative rates of reduction when equal volumes of permanganic acid are agitated, on the one hand, with a given volume of hydrogen, and on the other, with a quantity of the peroxide which is equal to that which should be produced by the absorption of the hydrogen. Here, again, the three solutions, A, B, and C, were employed in the comparison.

The quantities of permanganate to be reduced were in all cases 20 c.c. In addition to this, there was added to the hydrogen tubes a quantity of permanganate which would dispose of the gas in accordance with the equation $HMnO_4+3H=2H_2O+MnO_2$, and to the other tubes enough permanganate and manganous sulphate to produce the same amount of oxide as would result from the absorption of the hydrogen according to the equation $2KMnO_4+3MnSO_4+2H_2O=2HKSO_4+H_2SO_4+5MnO_2$. In adding the acid, account was taken of the fact that, in the case of those tubes in which the peroxide was produced by the action of the manganous salt on the permanganate, a portion of the required acid had already been introduced through the sulphate.

In order that the quantity of the gas introduced might be accurately measured, the tubes designed to receive the hydrogen were drawn out—at one end to a capillary, and at the other to a narrow neck—just wide enough to permit the introduction of liquids from a burette. After introducing the permanganate and the calculated amount of sulphuric acid, the larger passage was closed before the blast-lamp. The capillary end was then attached to a Hempel burette filled with mercury, and a volume of air was withdrawn from the tube which was equal to that of the hydrogen to be introduced. The burette was then replaced by one containing hydrogen. By careful manipulation no especial difficulty was experienced in introducing quite exactly the required volume of gas. To prevent the possibility of an explosion of the mixture of gases while closing the capillary, the tube was so inclined during the operation that the liquid in the tube covered the inner end of the narrow passage. It is hardly necessary to state that, in estimating the volume of gas required for an experiment, proper corrections were made for temperature, pressure, and water vapour.

Through the addition of sulphuric acid to all of the tubes, and of a standard solution of manganous sulphate to a portion of them, the original permanganate solutions were somewhat diluted, and those portions to which the manganous sulphate was added, to a greater extent than the others; hence, in order to equalise the conditions as to concentration, it was necessary to introduce a certain amount of water into the tubes in which the permanganate was to be agitated with hydrogen.

The tables which follow give the molecular ratio of the permanganic acid to be reduced to the oxide, the relation of the acid to the potassium of the permanganate, the time of agitation, the percentage reduction of the acid to peroxide, and the volumes of oxygen which were estimated to have been lost.

Permanganate Solution A.

1 c.c. equivalent to 5 m.grms. of iron.
Volume of original solution to be reduced = 20 c.c.
Volumes of hydrogen used = 7·5 c.c.
Molecular ratio of $HMnO_4 : MnO_2 = 20 : 12·5$.

It should be remarked with regard to the above, as well as all following similar data that, of the figures expressing reduction of permanganic acid, only those on the same horizontal line are safely comparable. This is true even when the time of agitation is the same in successive

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* From the *American Chemical Journal*, xx., No. 7.

Acid.	Time.	Decomposition by MnO_2 from $MnSO_4$.	Volume of oxygen liberated.	Decomposition by MnO_2 from H_2.	Volume of oxygen liberated.
	Hours.	Per cent.	C.c.	Per cent.	C.c.
K	150	13·75	0·83	9·59	0·58
K	150	16·50	0·99	8·55	0·51
K	300	21·67	1·29	10·25	0·62
K	600	40·00	2·40	14·34	0·86
2K	150	21·35	1·28	11·60	0·70
2K	150	17·65	1·06	14·00	0·74
2K	300	28·33	1·70	17·00	1·02
2K	300	28·33	1·70	16·67	1·00
2K	600	41·66	2·50	21·08	1·27
3K	150	15·16	0·91	15·83	0·95
3K	150	14·67	0·88	13·50	0·81
3K	300	26·34	1·58	20·83	1·25
3K	300	23·90	1·43	20·74	1·25
3K	600	44·91	2·70	27·00	1·62
3K	24	6·67	0·40	Hydrogen not all absorbed.	—
3K	24	5·25	0·32	,,	—

experiments, unless the agitation happened to be simultaneous. The rate of the reduction appears to be influenced even by such changes of temperature as are experienced in the laboratory, as, for instance, between day and night.

Permanganate Solution B.

1 c.c. equivalent to 10 m.grms. of iron.
Volume of original solution to be reduced = 20 c.c.
Volumes of hydrogen used = 15 c.c.
Molecular ratio of $HMnO_4 : MnO_2 = 20 : 12·5$.

Acid.	Time.	Decomposition by MnO_2 from $MnSO_4$.	Volume of oxygen liberated.	Decomposition by MnO_2 from H_2.	Volume of oxygen liberated.
	Hours.	Per cent.	C.c.	Per cent.	C.c.
3K	150	17·5	2·1	28·25	3·39
3K	150	15·08	1·81	27·33	3·21
3K	150	17·17	2·06	28·25	3·39
3K	300	33·17	3·98	31·75	3·80
3K	300	32·93	3·95	32·68	3·92
3K	600	61·59	7·38	43·75	5·25
3K	600	62·50	7·50	41·83	5·02
6K	150	18·18	2·18	32·50	3·90
6K	150	19·34	2·32	31·83	3·82
6K	150	20·18	2·42	35·08	4·21
6K	300	31·75	3·81	36·00	4·31
6K	300	31·75	3·81	37·08	4·45
6K	600	60·75	7·28	44·00	5·29
6K	600	75·75	9·08	46·43	5·57
3K	24	3·33	0·40	8·58	1·03
3K	24	4·00	0·48	10·67	1·28

Permanganate Solution C.

1 c.c. contained 51 m.grms. $KMnO_4$ = 89·38 m.grms. Fe.
Volume of original solution to be reduced = 20 c.c.
Volumes of hydrogen used = 40 c.c.
Molecular ratio of $HMnO_4 : MnO_2 = 20 : 3·784$.

Acid.	Time.	Decomposition by MnO_2 from $MnSO_4$.	Volume of oxygen liberated.	Decomposition by MnO_2 from H_2.	Volume of oxygen liberated.
	Hours.	Per cent.	C.c.	Per cent.	C.c.
K	150	9·68	10·48	19·93	21·58
K	150	13·75	14 90	19·93	21·58
K	300	22·59	24·38	21·58	23·39
K	300	17·00	18·42	21·75	23·57
2K	150	11·83	12·82	22·50	24·38
2K	150	12·68	13·73	23·93	25·92
2K	300	16·65	18·06	22·08	23·93
2K	300	20·93	22·66	23·33	25·28
3K	150	13·50	14·63	23·74	25·74
3K	150	12·93	14·00	25·83	27·99
3K	300	17·75	19·23	26·75	28·90
3K	24	2·50	2·71	19·58	21·22
3K	24	2·50	2·71	20·18	22·85

The relation of the reduction of the permanganic acid to the time of agitation, as well as to the acidity of the solutions, will be made clearer by the following arrangement, in which the means are given in the case of duplicated determinations:—

Solution A.

1. Oxide from $MnSO_4$.

	24 hours. Per cent.	150 hours. Per cent.	300 hours. Per cent.	600 hours. Per cent.
Acid = K	—	15·13	21·67	40·00
,, = 2K	—	19·50	28·33	41·66
,, = 3K	5·96	14·92	25·12	44·91

2. Oxide from H_2.

Acid = K	—	9·07	10·25	14·34
,, = 2K	—	12·08	16·84	21·08
,, = 3K	Hydrogen not all absorbed.	. . 14·67	20·79	27·00

Solution B.

1. Oxide from $MnSO_4$.

Acid = 3K	3·67	15·56	33·05	62·00
,, = 6K	—	19·23	31·75	68·27

2. Oxide from H_2.

Acid = 3K	9·63	27·94	32·22	42·79
,, = 6K	—	33·14	36·54	45·22

Solution C.

1. Oxide from $MnSO_4$.

Acid = K	—	11·72	19·75	—
,, = 2K	—	12·26	18·75	—
,, = 3K	2·50	13·22	17·75	—

2. Oxide from H_2.

Acid = K	—	19·93	21·67	—
,, = 2K	—	23·22	22·71	—
,, = 3K	19·88	24·82	26·75	—

An examination of the preceding table for the purpose of comparing the efficiency of manganous sulphate and hydrogen as oxygen liberating agents, shows that, in the case of solutions B and C, the latter is much more active than the former during the first twenty-four hours—that is, during the period of, or immediately following, the formation of the peroxide which results from the absorption of the gas. This is apparently not true of the very dilute solution A; for, in the experiments upon it, a somewhat smaller reduction of the acid was found than would have been accounted for by the complete absorption of the hydrogen. It cannot, however, be affirmed that the quantity of oxygen liberated was less, in proportion to hydrogen absorbed, in A than in B and C. This is one of the questions to which it is hoped to give further attention in the future. The maximum efficiency of the hydrogen as a quickly acting oxygen-liberating agent, appears to be reached in the case of the nearly saturated solution C, in which the mean reduction during the first twenty-four hours amounted to 19·88 per cent, as against 2·5 per cent for the manganous sulphate. We call attention to the fact—also noticeable in the results of Messrs. Meyer and Von Recklinghausen—that the reduction of 19·88 per cent signifies the liberation of 22 c.c. of oxygen, a volume which is nearly one-half that of the hydrogen (40 c.c.) employed in all the experiments with the solution C.

During the period from twenty-four hours to one hundred and fifty hours, the oxide produced by hydrogen acted much less rapidly in C than the oxide from the manganous salt. In B—and possibly also in A—the order of efficiency appears to be reversed, the oxide from the hydrogen being the more active one. The latter fact was interesting to us, because it may possibly throw some light upon the important question, whether the phenomenal liberation of oxygen which is observed when hydrogen or carbon monoxide acts upon permanganic acid, *attends the absorption* *of the gas or follows the formation of the oxide produced by the absorption of the same;* and it suggests a line of investigation which we hope to pursue.

During the period from one hundred and fifty to three hundred hours—also during that from three hundred to six hundred hours, wherever the agitation was so long continued—the oxide from the hydrogen was decidedly less active than that from the sulphate. In one instance, in which a portion of the solution C had been agitated with hydrogen for three hundred hours, a smaller reduction was found than had occurred in similar experiments during an agitation of one hundred and fifty hours. This discrepancy was explained at the time by the low temperature which prevailed during the agitation of the tube whose contents showed the low reduction.

Assuming that liberation of oxygen in solutions of permanganate or permanganic acid is in general due to the presence of suspended oxide, there is no evidence to be found in our results that the reaction has a limit, as believed by Messrs. Meyer and Von Recklinghausen. The evidence to the contrary is very clear in all cases in which the suspended oxide was prepared from manganous sulphate, and also in those cases in which the oxide from hydrogen acted upon solutions A and B. The reduction accomplished in C by the oxide from hydrogen is apparently small during the twenty-four to one hundred and fifty hour and the one hundred and fifty to three hundred hour periods. It is, however, unmistakable, except in the one case which has already been explained. That the percentage reduction for equal periods of time after the first twenty-four hours should be smaller throughout in C than A and B, is easily accounted for by the fact that the suspended oxide in C was relatively less than one-third of that in A and B.

The work which we have here described is only a fragment of a proposed investigation of the reduction of permanganic acid by the peroxide of manganese. The results obtained are not decisive; nor are they even strikingly important in their direct bearing on the question of the cause of the difference between the action of gaseous and liquid reducing agents on permanganic acid. They do, however, suggest certain possible methods of solving the problem.

SOME PRINCIPLES AND METHODS OF ANALYSIS APPLIED TO SILICATE ROCKS.[*]

By W. F. HILLEBRAND.

(Continued from p. 79).

Maganese, Nickel, Cobalt, Copper, Zinc.

Ammonia is added to the flask containing manganese, the earths, &c., and hydrogen sulphide gas is introduced, whereby manganese, nickel, copper, zinc, and a small part of the platinum from the dish are precipitated. The flask is set aside, corked for at least twelve hours, and preferably twenty-four, or even longer; the precipitate, collected and washed on a small filter with water containing ammonium chloride and sulphide, is extracted by hydrogen sulphide water acidified with one-fifth its volume of hydrochloric acid (sp. gr. 1·11), manganese and zinc, if present, going into solution.

Manganese.—The filtrate is evaporated to dryness, ammonium salts are destroyed by evaporation with a few few drops of sodium carbonate solution, hydrochloric and a drop of sulphurous acid are added to decompose excess of carbonate, and to dissolve precipitated manganese, and the latter is re-precipitated boiling by sodium carbonate after evaporation of the hydrochloric acid. If zinc is present it can be separated from the manganese after weighing. For the small quantities of manganese usually found the sodium carbonate method of precipitation is to be preferred to that by bromine or sodium phosphate, as equally accurate and a great time saver. No precipitations have as yet been made with hydrogen peroxide in alkaline solution, in the manner proposed by Jannasch and Cloedt (*Zeitschr. für Anorg. Chemie.*, vol. x., p. 405, 1895), but the method appears full of promise and extremely simple, affording also separation from zinc, if present, and it will be subjected to full trial at some future time.

The employment of ammonium sulphide instead of bromine for the separation of manganese from the alkaline earths and magnesia has the advantage that, by a single operation, nickel, copper, and zinc are likewise removed if present. There need be no fear of overlooking nickel or copper, for under the conditions of the precipitation they are not held in solution. Now and then a trace of alumina may be found in the precipitate, and magnesia, too, would contaminate it if ammonium salts were not present in sufficient quantity. Regard must therefore be had to these possibilities, and also to the rather remote possibility of the presence of rare earths which were not thrown out by the basic acetate precipitation (see footnote, p. 81).

Nickel, Cobalt, Copper.—The paper containing these is incinerated in porcelain, dissolved in a few drops of aqua regia, evaporated with hydrochloric acid, the copper and platinum thrown out warm by hydrogen sulphide, and nickel and cobalt thrown down from the ammoniacal filtrate by hydrogen sulphide. This is then rendered faintly acid by acetic acid and allowed to stand. The sulphide of nickel is simply burned and weighed as oxide, its weight being almost always very small, and then tested for cobalt in the borax bead.

It is somewhat unsafe to consider traces of copper found at this stage to belong to the rock if the evaporations have been conducted, as is usually the case on a copper water-bath, or if the water has been used which has been boiled in a copper kettle, even if tinned inside. Therefore, and because of its contamination by a little platinum, it is better to determine copper in a separate portion if its presence is indicated with certainty.

Calcium and Strontium (Barium).

Precipitation and Separation.—The platinum derived from the dish in the silica evaporation, except for the small portion precipitated with the manganese sulphide, is now wholly in the filtrate from the latter. Its filtration at this or any other stage is quite unnecessary; nor is the removal of ammonium chloride usually demanded, since there is no undue amount present in most cases, the first precipitation of alumina, &c., having been by sodium acetate.[*] Therefore, without destroying ammonium sulphide the calcium and strontium are thrown out by ammonium oxalate at boiling heat, the precipitate, often darkened by deposited platinum sulphide, is ignited and re-dissolved in hydrochloric acid, boiled with ammonia to throw out traces of alumina sometimes present, and re-precipitated as before, but in a small bulk of solution. It is weighed as oxide, transferred to a small flask of 20 c.c. capacity, dissolved in nitric acid, evaporated to dryness at 150° to 160° C., and the separation of strontium from calcium effected by ether-alcohol[†] or amyl alcohol (Browning, *Am. Journ. Sci.*, Series 3, vol. xliii., pp. 50, 314, 1892).

Behaviour of Barium.—Barium will, after two ammonium oxalate precipitations, never be found with the ignited calcium and strontium in more than spectroscopic traces, unless originally present in excess of 3 or 4 milligrms., and very often only when in considerable excess (W. F. Hillebrand, *Journ. Am. Chem. Soc.*, vol. xvi.,

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[*] From the *Bulletin of the United States Geological Survey*, No. 148, p. 15, 1897.

[*] If two or three precipitations by ammonia alone are depended on, the second and third filtrates are evaporated rapidly to dryness and the ammonium salts removed by ignition.

[†] See Fresenius, *Zeitschr. für Anal. Chemie*, vol. xxxii., pp. 189, 312, 1893, for the latest improvement in this method.

p. 83, 1894; Chemical News, vol. lxix., p. 147, 1894). If present with them, however, it will be separated with the strontium by ether-alcohol or amyl alcohol, and these two must then be treated by the ammonium chromate method as prescribed by Fresenius (*Zeitschr. fur Anal. Chem.*, vol. xxxix., p. 428, 1890), in order to arrive at the strontium. The barium is best estimated in a separate portion (see Barium).

Necessity of two Precipitations by Ammonium Oxalate.—It may be said with regard to the separation of calcium from magnesium, that two precipitations by ammonium oxalate are essential to the attainment of correct results, not only for the complete removal of magnesium but of sodium as well, the retention of compounds of the latter element by calcium oxalate having been frequently observed here and elsewhere.

Magnesium.

Platinum sulphide strongly contaminates the precipitate of magnesium phosphate in the first filtrate from the calcium oxalate, unless ammoniacal salts have been removed, as is advisable with very little magnesium; but this matters not, as it remains on the filter when the phosphate is re-dissolved in hydrochloric acid and added to the second filtrate from calcium oxalate, where it is again precipitated. Barium phosphate will not contaminate the second precipitate unless there are notable amounts of barium in the rock, in which case it must be removed by sulphuric acid prior to the final precipitation of the magnesium. The magnesium-ammonium-phosphate may be collected in a Gooch crucible and weighed, or on a paper filter, whence it may be washed into a tared crucible by nitric acid, evaporated,* ignited, and weighed therein as pyrophosphate. The latter way, though longer than that by the Gooch crucible, offers a certain advantage in facilitating the detection and estimation of the small amount of calcium which the magnesium always carries with it (see below), but it suffers from an objection which will appear shortly. In order to get the calcium which it carries the ignited pyrophosphate is dissolved in a few drops of hydrochloric acid, the solution is rendered just ammoniacal, the precipitate just re-dissolved by acetic acid, and a very small pinch of ammonium oxalate is added. In the cold solution, kept down to a few cubic centimetres in bulk, a turbidity appears shortly, which is almost invariably calcium oxalate, sometimes accompanied by magnesium oxalate. If necessary, it can be purified by re-solution and re-precipitation after ignition, and its weight, averaging one-half milligrm., is then added to that of the lime already found, and subtracted as tricalcium phosphate from that of the magnesium pyrophosphate, in order to arrive at the true figure for magnesium. This separation, to be successful, must be done with care.

Now it has been often observed that the pyrophosphate obtained by evaporation with nitric acid in a platinum crucible does not always dissolve completely in hydrochloric acid after ignition, but that sometimes a white residue is left in light lumps which appear to be quite insoluble in acids. It contains no silica, but only phosphoric acid and magnesia, apparently, and is presumably a peculiar metaphosphate. The cause of its formation is probably this: In the evaporation with nitric acid magnesium nitrate and free phosphoric acid are formed, and crystallisation partially takes place before the phosphoric acid has had a chance to expel the nitric acid, the consequence being that the complete molecular re-arrangement from which only pyrophosphate can result on ignition, can not take place, and the ignition product contains, in addition to pyrophosphate, other compounds, including, perhaps, metaphosphate and metaphosphoric acid. If the last, the weight found would be in error by the water retained by the metaphosphoric acid, even supposing none of the latter to be volatilised during ignition. Otherwise the weight would not differ from that of pyrophosphate alone. The uncertainty seems to be sufficient to condemn the method for accurate work, which is unfortunate, for it obviates the need of dissolving the phosphate off the felt of the Gooch crucible and subsequent concentration of the filtrate in order to look for contaminating lime.

Barium and Titanium.

Barium.—It has been said above (see preceding col.) that only in very exceptional cases will barium be found with the calcium and strontium after two, or possibly three, precipitations of the latter as oxalate, since it passes into the filtrates with the magnesium, whence it may be obtained as sulphate after the removal of ammoniacal salts. Addition of some alcohol insures also the recovery of traces of strontium if the rocks are very rich in it. But it is unsafe to regard the amount thus separated from the magnesium as representing the total amount of barium in the rock. It will almost always be found lower than the truth, probably for the reason that there are opportunities during the analysis for slight losses in the form of sulphate. It is best to estimate it in a separate portion, which may also serve with advantage for the estimation of titanium.

The powder is attacked by hydrofluoric and sulphuric acids, and every trace of the former then expelled by repeated evaporations with the latter. This expulsion of fluorine must be thorough, or else the titanium result will be low, and it is not always easy to effect this complete removal, though the time required seems to be in no slight degree dependent on the nature of the fluorides to be decomposed. Long after every trace of fluorine seems to be gone, the formation of a crust on the evaporating salts sometimes allows an accumulation of enough hydrofluoric acid gas to become plainly manifest to the smell on breaking the crust. Possibly fusion of the mixed sulphates and fluorides with boric acid, and removal of the latter by evaporations with methyl alcohol saturated with dry hydrochloric acid gas, as recommended by Jannasch (*Zeitsch. fur Anorg. Chemie.*, vol. xii., p. 223, 1896), for the conversion of sulphates and possibly fluorides into soluble chlorides, would effect this expulsion of fluorine more certainly than mere evaporation with sulphuric acid; but these operations evidently require almost constant personal supervision, whereas repeated evaporations with sulphuric acid can be carried out on a radiator with almost no supervision. Moreover, the barium would have to be re-precipitated, whereas by the sulphuric-acid method it is already as sulphate.

The sulphate residue is digested for some time with dilute sulphuric acid of not less than 5 per cent strength. With acid rocks solution is very complete, but it can be made nearly so with even the most basic by transference to a small beaker and boiling. The filtrate is set aside, the residue ignited and fused with sodium carbonate, since zircon, andalusite, and a few other minerals are incompletely decomposed by hydrofluoric acid, and zircon, at least, is often present in appreciable amount. The melt is leached with water, washed, and extracted by a few drops of dilute hydrochloric acid, from which solution the barium is thrown out by a large excess of sulphuric acid. A single solution of the barium sulphate in concentrated sulphuric acid and re-precipitation by water suffices to remove traces of calcium which might contaminate it if the rock was one rich in calcium, and even strontium is seldom retained by it in quantity sufficient to be concerned about. Should this be the case, however, which will occur when the SrO and BaO are together in the rock in, roughly speaking, 0·2 and 0·4 per cent respectively, the only satisfactory way is to convert the sulphates into chlorides and to apply to the mixture the ammonium chromate method of separation (see *ante*).

Barium and strontium sulphates can be brought into a condition for testing spectroscopically by reducing for a very few moments the whole or part of the precipitate on

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* A pink colour of varying intensity almost invariably becomes apparent as the mass approaches dryness, a most delicate test for the traces of manganese which always escape precipitation by ammonium sulphide or bromine.

a platinum wire in the luminous tip of a Bunsen burner, and then moistening with hydrochloric acid. This should be known to everyone, but probably is not.

The procedure outlined in the foregoing paragraphs for the estimation of calcium, strontium, and barium in silicate rocks is the one which long experience has shown to be best adapted for securing the most satisfactory results with a minimum expenditure of time (for details consult W. F. Hillebrand, *Journ. Am. Chem. Soc.*, vol xvi., p. 83, 1894; Chemical News, vol. lxix., p. 147, 1894). Even where no attempt is made to separate contaminating traces of SrO and BaO one from the other, the error is usually of no great consequence, for an absolute error of 25 per cent, even in a substance constituting only one or two tenths per cent of a rock is ordinarily of small moment compared with the ability to certify to its presence with approximate correctness.

Separation of Barium from Calcium and Magnesium by the Method of Mar.—With such small amounts of barium as are usually found in rocks it is doubtful if Mar's (*Am. Journ. Sci.*, Series 3, vol. xliii., p. 521, 1892) method for the separation of barium from calcium and magnesium, by the solvent action of concentrated hydrochloric acid mixed with 10 per cent of ether on the chlorides, could be conveniently applied here, although for larger amounts the method would seem to be accurate, and easily executed. Moreover, it would probably not entirely remove contaminating strontium, and hence offers no advantage.

Titanium: Colorimetric Method.—The small hydrochloric filtrate from the barium sulphate, above mentioned, is evaporated to expulsion of the hydrochloric acid and added to the main solution containing the titanium, which is then oxidised by fluorine-free hydrogen peroxide (W. F. Hillebrand, *Journ. Am. Chem. Soc.*, vol. xvii., 1895; Chemical News, vol. lxxii., p. 158, 1895), and compared with a standard solution of titanium sulphate, similarly oxidised (Weller's method) (*Ber. Deutsch. Chem. Gesell.*, vol. xv., p. 2593, 1882). Mere traces of hydrofluoric acid render the results inaccurate; hence the caution enjoined as to the first treatment of the rock powder and as to the character of the hydrogen peroxide, which, as sold in the market, often contains fluorine.

Dunnington (*Journ. Am. Chem. Soc.*, vol. xiii., p. 210, 1891) has pointed out the necessity for the presence of at least 5 per cent of sulphuric acid in solutions which are to be thus tested for titanium, in order, as he concludes, to prevent partial reversion to metatitanic acid, which does not give a colour with hydrogen peroxide. The standard solution of titanium sulphate holding conveniently about 1 centigrm. TiO_2 in 10 c.c., equivalent to 1 per cent of TiO_2 in 1 grm. of rock, contains, therefore, 5 per cent or more of sulphuric acid. Of this, 10 c.c. are mixed with a sufficiency of hydrogen peroxide (2 c.c. of most commercial brands is ample) and diluted to 100 c.c. in a measuring flask.

The solution to be tested, evaporated if necessary to less than 100 c.c., is now to be fully oxidised, and if the colour is less intense than that of the standard, is made up to 100 c.c. with dilute sulphuric acid in a measuring flask, and mixed, otherwise in a flask of sufficient size to insure that its colour shall be less intense. If rectangular cylinders are used for comparison, there should be a light box, blackened inside and provided with one ground-glass end against which the cylinders can be sunk from an opening above, the other end being open for the observer to look through. One cylinder being filled with the solution to be tested, 10 c.c. of the diluted standard are run into the other from a burette, and water is added from a second burette until there is no distinction as to colour. A second and a third portion of the standard can be run in and diluted, and the mean of several determinations struck, when a simple calculation gives the percentage of TiO_2 in the rock.

If the convenient but expensive Soleil-Duboscq colorimeter is used, or the simple Nessler tubes, it is of course unnecessary to dilute the rock solution to the extent above required, should it be stronger than the standard. Experience has shown, however, that differences can not be sharply estimated in strongly coloured solutions, and that the results are much more satisfactory when the colour intensity is not much, if any, greater than that given by a standard of the above concentration. For the percentages of titanium found in rocks, clays, and soils, usually under 1 per cent, but rising to 2 or even 3 per cent or more occasionally, the colorimeter method gives results which are fully equal to those of the best gravimetric method, besides being a great time saver. The error introduced by iron, in consequence of the yellowish colour of its sulphate solution, is practically negligible unless its percentage is very high; then either the iron must be removed prior to making the colour test or, possibly better still, correction should be applied for known amounts of ferric sulphate in solutions of the requisite dilution.

The exact correction to be applied in such cases is difficult of determination because of the impossibility of matching the colours of titanium peroxide solutions with those of ferric sulphate; but tests made go to show that the colouring effect of 0·1 grm. of Fe_2O_3 in 100 c.c. 5 per cent sulphuric acid solution is about equal to 0·2 m.grm. of TiO_2 in 100 c.c. when oxidised by hydrogen peroxide. This amounts to a correction of only 0·02 per cent on 1 grm. of rock containing the unusual amount of 10 per cent Fe_2O_3.

Gooch's Method not readily Applicable to Rocks Containing Zirconium.—Prior to the adoption of this method, the excellent one of Dr. Gooch (*Proc. Am. Acad. Arts Sci.*, N.S., vol. xii., p. 435; *Bull. U.S. Geol. Survey*, No. 27, p. 16; Chemical News, vol. lii., pp. 55 and 68, 1885), was invariably used in this laboratory. Occasional inability to secure clean and complete precipitations by it was experienced, especially with a certain series of rocks rather poor in titanium. Long research showed the difficulty to be due to the presence of zirconium, which acts as a marked preventive of the precipitation of titanium by boiling in an acetic acid solution. The above rocks were found to contain up to 0·2 per cent of ZrO_2, and this amount was able to prevent precipitation of 0·3 per cent of TiO_2. The titanium which came down in excess of this amount did not settle out in flocculent condition, as happens when zirconium is not present, and it was difficult to filter. After the removal of the zirconium, however, no difficulty was experienced in precipitating all the titanium with the usual ease. In view of the good results obtainable by the colorimeter method in the presence, and by the Gooch method in the absence, of zirconium, it is incomprehensible that the old method of precipitation by many hours boiling in a nearly neutral sulphate solution in presence of sulphurous acid should still find adherents in any part of the world.

Baskerville's Method.—Baskerville (*Journ. Am. Chem. Soc.*, vol. xvi., p. 427, 1894), has proposed the separation of titanium from iron and aluminum by boiling the neutralised solution of the chlorides for a few minutes in presence of sulphurous acid. The test separations, as given by him, are sharp, and a single precipitation is said to suffice, the titanium being found free from iron and easily filterable. If it is desired to determine TiO_2 gravimetrically, this method seems admirably suited. Zirconium would probably be likewise precipitated (see *prox.*), and phosphorus, perhaps, also; but this last point has not been investigated.

(To be continued).

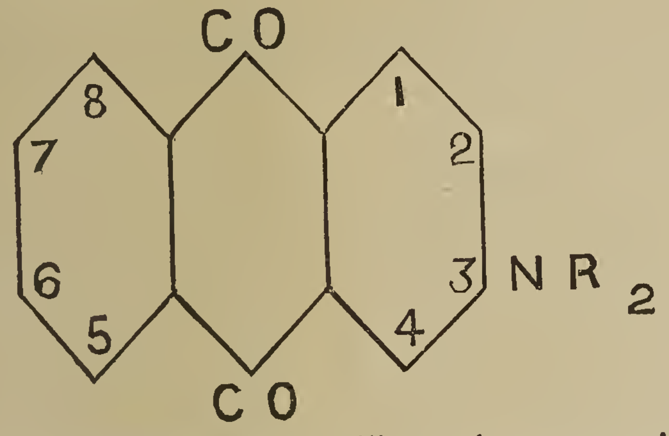
The Molecular Transposition of the Ethers of some Iso-aldoximes. — C. Neubauer. — β-Mononitrobenzaldoxime gives, with the mononitrobenzaldehyd in alcoholic solution, mononitrobenzyl-mononitro-isobenzaldoxime, $C_{14}H_{11}N_3O_3$. Benzyliso - œnantaldoxime, $C_{14}H_{21}NO$, which melts at 78°, undergoes only a doubtful transformation or even none at all. A number of other bodies are described, and the author finishes with a few remarks on the preparation of benzhydroxylamine.—*Liebig's Annalen.*

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvi., No. 22, May 31, 1898.

The Preparation and Properties of the Dialcoylamido-anthraquinones-3.—A. Haller and A. Guyot.—The authors have already shown that the substituted orthobenzoylbenzoic acids are transformed by the influence of reducing agents, first into substituted monophenylphthalides, and then into the benzylbenzoic derivatives. They have now endeavoured to condense these acids into anthraquinonic compounds by the method used for producing analogous compounds with the benzoylbenzoic acids. By heating dimethyl-anidised acid with concentrated sulphuric acid at 175°—180° sulphurous acid is given off, and eventually—after precipitation, washing, &c.—beautiful red needles are formed, melting at 181°. Besides this dimethylamidoanthraquinone, there are always present badly-defined products of oxidation. These have been studied, with the result that the method adopted for the condensation has been modified. The new anthraquinonic derivatives can only have the following constitution:—

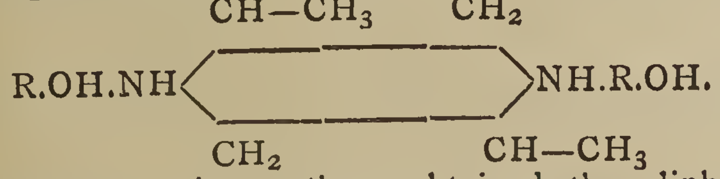


They lend themselves very readily to the preparation of a group of nitrated, amidised, sulphonated, and hydroxylised derivatives, of which some may be applied to the arts.

Action of some Carbonates on Chromous Acetate.—G. Bauge.—Already inserted in full.

The State of Equilibrium of the Ternary System: Lead—Tin—Bismuth.—Georges Charpy.—These three metals are capable of mixing in all proportions, and form at the requisite temperature a homogeneous liquid; they do not form definite compounds or isomorphous solutions, solids, or mixtures. They therefore correspond to the simplest case that can be presented from the point of view of chemical equilibrium. The composition of any such an alloy can be shown diagrammatically by means of the Thurston triangle. A point taken within this triangle represents the ternary alloy which contains quantities of the three metals proportional to the distances of this point from the three sides of the triangle. Here a good deal of mathematics follows.

On Dimethylpiperazine and some Phenolic Combinations of this Base.—P. Cazeneuve and M. Moreau.—When heated in alcohol at 93°, molecule for molecule, under the same conditions as piperazine, dimethylpiperazine disengages carbonic acid at the expense of the phenolic carbonates, and we finally obtain, instead of urethanes, diphenolic combinations of the base corresponding to the general formula:—



$$\mathrm{R.OH.NH}\left\langle\begin{array}{cc}\mathrm{CH{-}CH_3} & \mathrm{CH_2}\\ \mathrm{CH_2} & \mathrm{CH{-}CH_3}\end{array}\right\rangle\mathrm{NH.R.OH.}$$

In this manner the authors obtained the diphenate, digaïacolate, and the dinaphtholates α and β of dimethylpiperazine. This new base, by reason of its recent introduction into therapeutics (lycetal, or tartrate of dimethylpiperazine), merits further study, so that its properties may the better be understood.

Heats of Neutralisation of Phenylphosphoric Acid.—G. Belugou.—The product of the reaction of phosphoric anhydride on phenol is dissolved in water and washed with ether to remove the diphenyl-phosphoric acid. The aqueous solution is treated with acetate of lead. Fractional precipitations enable us to separate the phosphoric acid, which is the first precipitated. The monophenyl phosphate of lead, which is next formed, is suspended in water and decomposed by sulphuretted hydrogen. By adding small portions of the salt to a known volume of water the richness of the solution can be determined by simple acidimetry; when the solution contains 1 molecule of phenylphosphoric acid per 6 litres it is neutralised and the carbon determined.

Some Halogen Derivatives of Ethylphenylketone.—A. Collet.—The halogen derivatives described in this note were obtained by the action of the chlorides of propionyl and of α-bromoproprionyl on monochlorised or monobromised benzene in the presence of $AlCl_3$. The operation is conducted in the same manner as in the case of the halogen derivatives of methylphenylketone. Four of these derivatives are fully described, viz., ethyl-*p*-chlorophenylketone, ethyl-*p*-bromophenylketone, bromoethyl-*p*-chlorophenylketone, and bromoethyl-*p*-bromophenylketone.

Bulletin de la Société Chimique de Paris. Series 3, Vol. xix.-xx., No. 8.

Conductivity of Electrolytes in Organic Solutions.—P. Dutoit and L. Friderich.—A very long paper, in which the authors describe a number of experiments with various organic substances; they finally conclude that the values $\mu\infty$, furnished by the same electrolyte dissolved in different solvents, are in direct function of the degree of polymerisation, and in inverse function of the coefficient of viscosity of these solvents.

Speed of Limited Reactions.—P. Th. Muller.—A chemical reaction is limited when it stops before the whole of the substance theoretically transformable has undergone the change indicated by the chemical equation. The authors have studied the subject of etherification of acetic acid and alcohol in equivalent quantities at the ordinary temperature, also by Knoslauch's method, as well as that of saponification; these are all treated mathematically, but, the authors add, it does not appear possible to represent all cases of etherification by formulæ when the reaction is between equivalent quantities of acids and alcohols; the acid plays a preponderating part and the equilateral hyperbola proposed by M. Berthelot shows the speed of the reaction with the greatest fidelity.

Absorption of Nitric Oxide by Ferrous Salts.—V. Thomas.—Already inserted in full.

The Action of the Bacteria of Sorbase on the Plurivalent Alcohols.—G. Bertrand.—It has already been shown by the author that sorbite can be transformed into sorbase by the action of a particular bacterium. MM. Vincent and Delachanal have, with the same bacterium, obtained levulose from mannite. These two tranformations are absolutely comparable; they correspond to the production of a ketose by the oxidation of a secondary alcoholic grouping of the primitive body, and the same formula of the reaction serves to represent them both. The plurivalent alcohols experimented on are divided into two groups; some—such as glycol, xylite, and dulcite—resist the oxidising action, while others on the contrary—particularly glycerin, sorbite, and mannite, of which the coefficient of carbon is a multiple of three—contribute in a most efficacious manner to the growth of the microbe, at the same time losing 2 atoms of hydrogen, forming, besides the two bodies already mentioned, erythrite, arabite, volemite, and perseite.

Note on the Formation of Aromatic Fatty Ketones by the aid of Chloride of Aluminium.—J. Boeseken.—The ordinary method of preparing the aromatic fatty ketones by the condensation of the aromatic hydrocarbides with the chlorides of the acids by the aid of chloride of aluminium gives but poor results; by taking care to use freshly prepared chloride of aluminium, *always in excess*, and not allowing the reaction to last too long, the author has succeeded in obtaining almost theoretical results. The product of the reaction is almost colourless, and the quantity of pure ketone obtained varies from 85 to 97 per cent of the carbide used.

On Camphor and its Derivatives.—G. Blanc.—A very long paper, not capable of useful abstraction.

On the Essence of Portugal.—J. Flatau and H. Labbé.—In the latest work on essence of Portugal (sweet oranges) myristic acid and myristicol have been found to be present. A new ether has also now been found; it has a very agreeable odour, very characteristic of oranges. It melts at 64° to 65°, and is easily soluble in ether, benzene, and chloroform in the cold, difficultly so in warm alcohol; it is almost insoluble in cold alcohol, light ligroin, and boiling water. In an etherised solution a large quantity of bromine is absorbed; after driving off the ether and washing with cold alcohol we obtain a pale yellowish powder, melting at 56° to 57°, easily soluble in ether, cold benzene, and chloroform, and insoluble in ligroin and boiling alcohol. Analysis shows the presence of a large quantity of bromine in the molecule of this new compound.

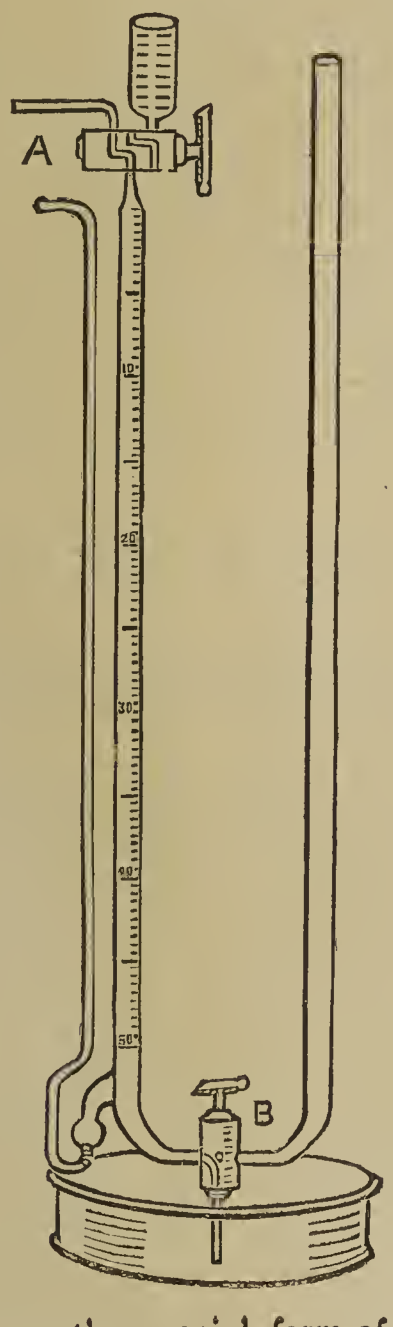
THE CHEMICAL NEWS.

Vol. LXXVIII., No. 2022.

ON A MODIFIED FORM OF NITROMETER FOR USE IN NITROGEN ESTIMATIONS BY THE ABSOLUTE METHOD.

By H. A. D. JOWETT, D.Sc. and F. H. CARR, A.I.C.

During the progress of the investigation of the aconite alkaloids it was necessary to conduct a large number of determinations of nitrogen by the absolute method, and to examine chemically the gas so obtained (Jowett, *Trans. C. S.*., 1896, p. 1524; Dunstan and Carr, *Proc. C. S.*, 1896, p. 48).



For this purpose the special form of nitrometer to be described was designed. An extended experience with it has made manifest so many points in which it is superior, in our opinion, to other forms that it has been thought desirable to give a brief description of the apparatus.

The construction of the nitrometer is simple and the diagram hardly needs further explanation.

In using the apparatus the nozzle of the tap B is kept immersed in the potash solution contained in the dish, and the tap is turned so that the potash is expelled through this nozzle by the incoming gas.

When it is desired to read the volume of the gas, the liquid in the two columns is brought to the same level by use of the three-way tap B.

The advantages gained by the use of this nitrometer over other forms, when indiarubber tubing is not used, may be briefly summarised as follows:—

1. The gas may be readily washed by allowing potash solution to flow through the apparatus: this enables the measuring limb to be of small capacity, and capable of more accurate reading than is common with most nitrometers. In this case there is no fear of the potash solution becoming saturated with carbonic anhydride, and thus spoiling the combustion.

It has been our custom to keep a gentle stream of potash flowing during a combustion, re-filling the cup at intervals.

2. By working under considerably diminished pressure an even current of gas can more readily be maintained, and the risk of bursting the heated tube is lessened.
3. The gas may be drawn off for subsequent analysis.
4. It is usual in a combustion to first pass carbonic anhydride through the tube to drive out all the air, and the frequent testing of the gas to see if all the air is expelled necessitates — in the ordinary Schwarz's nitrometer—the filling and emptying of the potash in the side limb, an operation which is entirely avoided in the use of the nitrometer now described.

The apparatus is not much more expensive than the ordinary form of nitrometer, and could readily be obtained from any instrument maker.

ON THE SYNTHESIS OF ALBUMIN.

By ALFRED H. ALLEN.

The announcement of Dr. Leo Lilienfeld at the recent International Congress of Applied Chemistry at Vienna, that he had effected the synthesis of albumin, will be received by chemists with considerably more scepticism than it has met at the hands of the professional paragraphists. The circumstances of the announcement are not such as to encourage implicit faith in the reality of the alleged discovery, but Dr. Lilienfeld may be the victim in this respect of the professional zeal of the reporter.

From the accounts which have hitherto come to hand, it appears that it is not true albumin of which Dr. Lilienfeld claims to have effected the synthesis, but "peptone," which is a very different thing. It is said to be produced by the condensation of glycocine (amido-acetic acid) with phenol, by means of phosphorus oxychloride. The reaction is said to occur quantitatively and with great facility, allowing of the whole process being shown at the meeting. Further, Dr. Lilienfeld is said to have demonstrated, by the most conclusive tests, the absolute identity of his product with natural peptone, or—according to some accounts—with true albumin. Seeing how very ill-defined are the chemical tests for "peptone," and that more than one kind of peptone is recognised, this part of the account must be received with caution. Still more doubt attaches to the statement that Dr. Lilienfeld's product has the same elementary composition as natural peptone (or albumin). Seeing that natural albumin and peptone both contain sulphur as an essential constituent, and that Dr. Lilienfeld's process does not involve the employment of sulphur in any form, there seems to be a screw very loose somewhere.

Although the description of the mode of formation of Lilienfeld's body appears to negative the conclusion that he has effected the synthesis of either albumin or peptone, it by no means follows that he has not produced an albuminoid substance of great theoretical interest. He has undoubtedly been working in the right direction—in fact, his method may not improbably have been suggested by the interesting and ingenious suggestions of Dr. P. W. Latham (Croonian Lectures, 1886).

Commencing with the fact that by the reaction of hydrocyanic acid on aldehyd, cyan-ethylic alcohol,—

$$CH_2.CH(CN).OH,$$

is formed, Latham points out that the cyan-alcohols are, as a class, very unstable bodies, readily undergoing change, and when treated with ammonia form unstable cyan-amides, which easily undergo condensation with formation of imido-nitriles and elimination of ammonia. Latham thinks these facts suggest the enquiry :—"Have we not in these cyanogen compounds substances possessing some properties that belong to living tissue, namely, those of undergoing intra-molecular change and also condensation? And, further, if from these substances we can obtain the various products which result from the disintegration of albumin, may not albumin itself be simply a compound made up of these elements?"

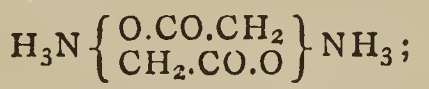
In the laboratory, it is practicable to obtain from these cyan-alcohols the corresponding amido-acids, glycocine, leucine, &c.,* and all the acids of the acetic and lactic series. Latham suggests that, if it were found possible to reverse the process, albumin might be built up theoretically from such constituents.

Latham further instances the well-known molecular transposition by which ammonium cyanate is converted into urea, and quotes Pflüger's remark that the great molecular energy of cyanogen compounds suggests that the functional metabolism of protoplasm by which energy is set free may be compared to the conversion of the energetic unstable cyanogen compounds into the less energetic and more stable amides. In other words, that *ammonium cyanate* is a type of living, and *urea* of dead, nitrogen, and that the conversion of the former into the latter is an image of the essential change which takes place when a living proteid dies.

In accordance with this view, the group $-CO.NH-$ is dead nitrogen, and would, on becoming part of a living tissue, be transformed into $=C:N.OH$.

Cyanic acid, CNOH, is itself readily susceptible of polymerisation, with formation of cyamelide, $C_3H_3N_3O_3$.

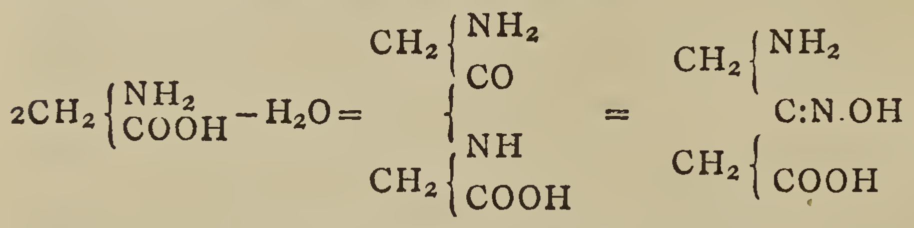
Latham points out that the glycines are capable of uniting with each other, glycocine being not improbably glycocine amidoacetate,—



$$H_3N\left\{\begin{matrix}O.CO.CH_2\\CH_2.CO.O\end{matrix}\right\}NH_3;$$

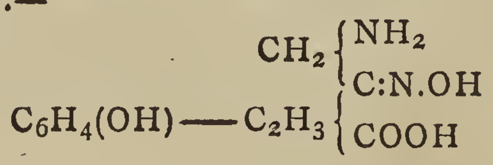
and that by the dehydration of this and allied bodies, cyan alcohols might be formed.

Thus, a double molecule of glycocine by dehydration would give a substance which might contain either a CO.NH group or a C:N.OH group, according to the arrangement of the atoms in the molecule.



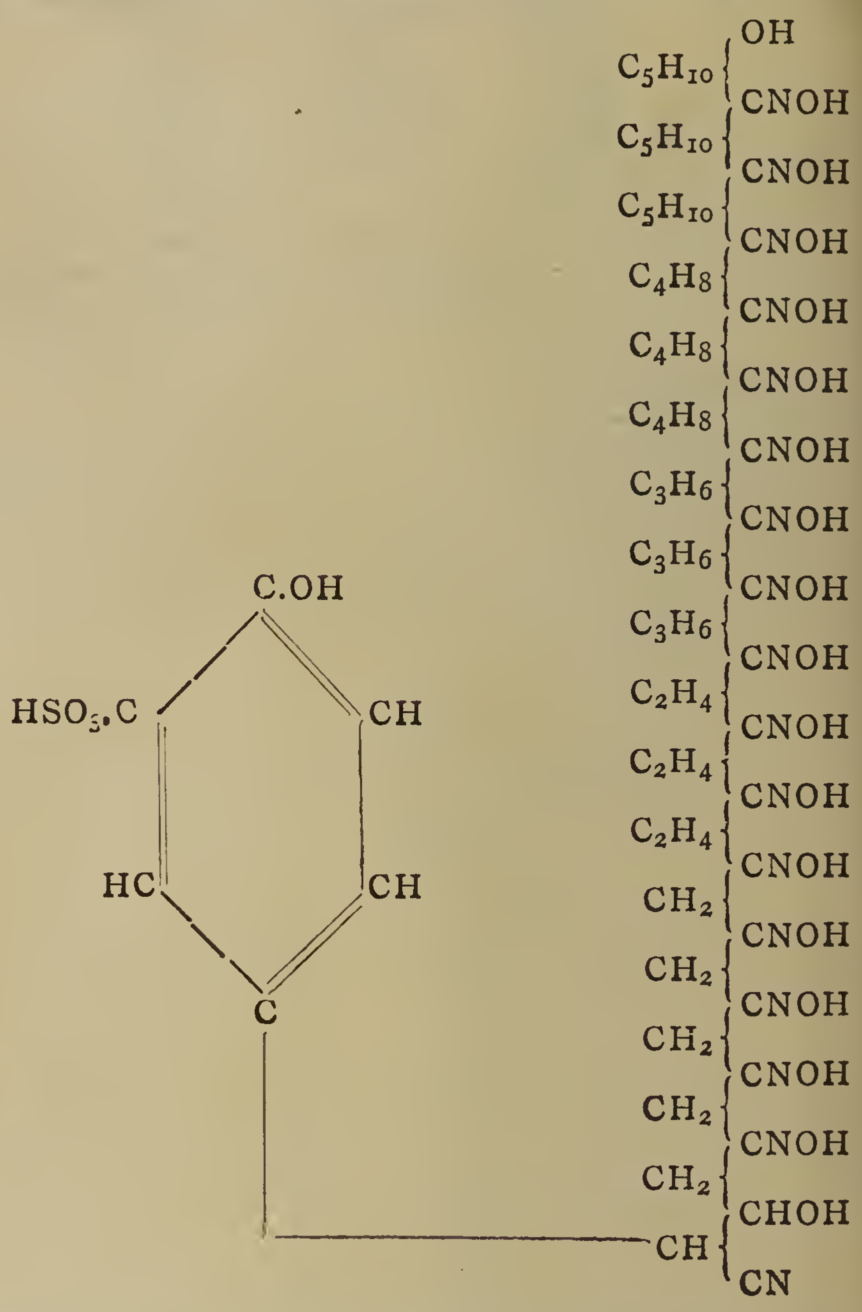
$$2CH_2\left\{\begin{matrix}NH_2\\COOH\end{matrix}\right.-H_2O=\begin{matrix}CH_2\left\{\begin{matrix}NH_2\\CO\end{matrix}\right.\\ \left\{\begin{matrix}\\ \end{matrix}\right.\\ CH_2\left\{\begin{matrix}NH\\COOH\end{matrix}\right.\end{matrix}=\begin{matrix}CH_2\left\{NH_2\right.\\ C:N.OH\\ CH_2\left\{COOH\right.\end{matrix}$$

Tyrosine is a member of the glycine group, and has the constitution of a para-hydroxyphenyl-amidopropionic acid. Latham shows that, by coalescence with glycocine and elimination of water, it would yield a body of the following constitution :—



$$\begin{matrix} & CH_2\left\{\begin{matrix}NH_2\\ \end{matrix}\right.\\ & C:N.OH\\ C_6H_4(OH)-\!\!-C_2H_3 & \left\{COOH\right.\end{matrix}$$

By similar ingenious reasoning, Latham shows how such a body as taurine may be introduced into the molecule, and he finally builds up the following formula as possibly representing the constitution of albumin :—



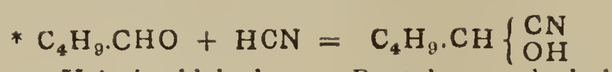
This suggestive formula contains $C_{72}H_{118}N_{18}O_{22}S$, and differs only by H_6 from Lieberkühn's formula for albumin, $C_{72}H_{112}N_{18}O_{22}S$.

The discovery of lysine, lysatine, and trypsophan or protein-chromogen, necessitates some modification of the above formula, which, of course, cannot be regarded as more than an ingenious and highly suggestive arrangement, which might be of service as a working hypothesis.

Pflüger has observed, and Loew and Bokorny corroborated the fact, that living proteid matter in the cells of various algæ reduces silver from a dilute alkaline solution of the nitrate, but that dead protoplasm or proteid does not give the reaction. Hence it is suggested that a compound of aldehydic nature exists in living protoplasm. By the reaction of formic aldehyd with ammonia, aspartic aldehyd may be supposed to be formed, a body which, though unknown, has the same composition as leucine. By its repeated polymerisation in presence of hydrogen and a sulphur compound, with elimination of water, the following equation may be realised :—

$$6C_{12}H_{17}N_3O_4+H_2S+6H_2=C_{72}H_{112}N_{18}SO_{22}+2H_2O.$$

Grimaux (*Compt. Rend.*, xciii., 771) has proposed to define proteids as "nitrogenised colloids, which by hydrolysis split up into amidated acids, carbon dioxide, and ammonia." On heating aspartic anhydride to 130° with urea for two hours, Grimaux obtained a thick mass, completely soluble in boiling water to a gummy, highly colloid liquid, yielding highly gelatinous precipitates with acids, alkaline salts, magnesium and aluminium sulphates, solutions of iron, copper, and mercury, and with tannin. The jelly yielded by acetic acid dried up to a substance resembling dried albumin. It softened in boiling water without undergoing solution, but dissolved in caustic potash to a liquid giving a violet colouration with cupric sulphate.



$$* \; C_4H_9.CHO + HCN = C_4H_9.CH\left\{\begin{matrix}CN\\OH\end{matrix}\right.$$

Valeric aldehyd. Pentyl cyan-alcohol.

$$C_4H_9.CH\left\{\begin{matrix}CN\\OH\end{matrix}\right. + NH_3 = C_4H_9.CH\left\{\begin{matrix}CN\\NH_2\end{matrix}\right.+H_2O$$

Pentyl cyan-alcohol. Pentyl cyan-amide.

$$C_4H_9.CH\left\{\begin{matrix}CN\\NH_2\end{matrix}\right. + 2H_2O = C_4H_9.CH\left\{\begin{matrix}COOH\\NH_2\end{matrix}\right. + NH_3$$

Pentyl cyan-amide. Leucine.

Of course it by no means follows, as Dr. Lilienfeld is reported to have said, that a synthetical product of the same ultimate composition as peptone will have the same food-value. This fact is familiar to the mere tyro; but it may be of interest to recall the case of quinine, the synthesis of which may any day be effected. Already two distinct basic substances isomeric with quinine have been prepared synthetically, but neither base has the physiological characters of true quinine.

Sheffield, August 13, 1898.

SIXTEENTH ANNUAL REPORT OF THE COMMITTEE ON INDEXING CHEMICAL LITERATURE.*

The Committee on Indexing Chemical Literature respectfully presents to the Chemical Section its Sixteenth Annual Report, covering the twelve months ending August, 1898.

Works Published.

"A Bibliography of the Metals of the Platinum Group," —Platinum, Palladium, Iridium, Rhodium, Osmium, Ruthenium, 1748—1896. By Jas. Lewis Howe, Smithsonian Miscellaneous Collections, 1084. City of Washington, 1897. Pp. 318, 8vo.

This fine volume forms one of the most valuable and comprehensive indexes to an important field of chemical literature produced under the auspices of the Committee since its appointment in 1882. It shows on every page evidence of conscientious and critical skill; the author- and subject-indexes, with which the book concludes, are important features. Its workmanship and the method of presentation of data in type make Dr. Howe's volume a model.

"References to the Literature of the Sugar-Beet," exclusive of works in foreign languages. By Claribel Ruth Barnett. U.S. Department of Agriculture. Library Bulletin, June, 1897. 9 pp. 4to.

This carefully edited contribution to the bibliography of a subject interesting to the chemist as well as to the scientific farmer, manifests the activity of the U.S. Department of Agriculture in its Library.

"A Chemical Bibliography of Morphine, 1875—1896." By H. E. Brown, under the direction of A. B. Prescott. Completed in "Pharmaceutical Archives," vol. i., No. 3.

A supplement carries the literature through 1897. The separates contain an index of authors.

"A Bibliography of the Metallography of Iron and Steel." By Albert Ladd Colby. Published in the *Metallographist*, vol. i., No. 2, pp. 168—178, April. 1898.

This includes 188 titles, arranged alphabetically by authors, and numbered chronologically; it is reprinted, extended, and re-arranged from *The Iron Age*, Jan. 27, 1898, by the author.

"Review and Bibliography of the Metallic Carbides." By J. A. Mathews. *Smithsonian Miscellaneous Collections*, No. 1090. City of Washington, 1898. Pp. 32, 8vo.

Published by the Smithsonian Institution on recommendation of this Committee. Under each metal forming a carbide the author has given a brief synopsis of the chemical data with references to the literature on that subject. There is an author-index.

"A Catalogue of Scientific and Technical Periodicals, 1665—1895, together with Chronological Tables and a Library Check-List." By Henry Carrington Bolton. Second edition. *Smithsonian Miscellaneous Collections*, No. 1076. City of Washington. 1897. Pp. 1247. 8vo.

This bibliography was first issued in 1885, and the second edition has been prepared at the request of the Smithsonian Institution. It embraces periodicals in every department of pure and applied science, including of course chemistry and chemical technology. The Chronological Tables give the date of publication of each volume of about 550 periodicals; they enable one to ascertain the date of a given volume in a given series of a given work, or to determine the number of a volume when the date only is given. The Library Check-List shows in what American Libraries, 133 in number, complete sets of the periodicals may be found. The second edition brings the date down to 1895; its publication has been delayed by the compilation of the Check-List. The periodicals catalogued number 8603.

"Alkaloidal Estimation;" a bibliographical index of chemical research prepared from original literature for the Committee of Revision and Publication of the Pharmacopœia of the United States of America, 1890—1900, by Paul I. Murrill under the direction of Albert B. Prescott. Ann Arbor, 1898.

A pamphlet of about sixty pages, not for sale.

"The Review of American Chemical Research," edited by Arthur A. Noyes and published in the *Journal of the American Chemical Society*, completed vol. iii., in December, 1897. Two indexes, an author- and a subject-index, increase its value.

Mr. E. W. Allen, Acting Director of the Office of Experiment Stations, U.S. Department of Agriculture, in reply to inquiries, sends the following communication:—

"During the past year we have completed volume ix. of the 'Experiment Station Record' (1897—'98). This, like former volumes, contains abstracts of and references to articles on the methods and results of work in agricultural chemistry published in this country and in Europe. During the past year the review of Russian scientific periodicals has been added. About 2000 cards of the Card Index of Experiment Station Literature have been issued during the past year, making a total of 16,000 cards in this index at present. In addition to several accounts of chemical studies of the nutrition of man, the Office has issued a 'Report of Preliminary Investigations on the Metabolism of Nitrogen and Carbon in the Human Organism with a Respiration Calorimeter of Special Construction,' by W. O. Atwater, C. D. Woods, and F. C. Benedict, the work being carried on in part by funds furnished by this Office. In this connection may also be mentioned a compilation of over 400 pages of metabolism experiments in which the balance of income and outgo was determined, made by W. O. Atwater and C. F. Langworthy, and issued from this Office. The bulletin is a digest of about 3600 experiments with man and animals, in which the balance of one or more of the factors of income and outgo was determined. While this work may at first thought seem somewhat a field, it is chemical in its character as well as physiological, and has involved in some cases quite extensive chemical studies."

The "Digest of Metabolism Experiments" herein named forms Bulletin No. 45 of the Office of Experiment Stations, and constitutes a comprehensive bibliography of the subject.

The Committee chronicles the publication of the following bibliographies bearing more or less on chemical researches:—

"Contributions to the Bibliography of Gold." By A. Liversidge. Australasian Association for the Advancement of Science. Brisbane, 1895, 8vo.

"Analyst" (The). The organ of the Society of Public Analysts. General Index to the *Proceedings of the Society of Public Analysts*, vol. i. (1876), and to the

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* From Advance sheets of the *Proceedings of the American Association for the Advancement of Science*, August meeting, Boston, 1898. Communicated by H. Carrington Bolton.

Analyst, vols. i.—xx. (1877—1896). Compiled by J. Cuthbert Welch. London, 1897. Pp. i.—181, 8vo.

Arranged on the dictionary plan, authors, subjects, and cross-references in a single alphabet.

"Bibliographie des Travaux Scientifiques" (Sciences Mathématiques, Physiques, et Naturelles), publiés par les Sociétés Savantes de la France. Par J. Deniker. Tome 1, part 2. Paris, 1897, 4to.

Part 1 was published in 1895. Most important for original papers published in France.

"Biographisch - Literarisches Handwörterbuch zur Geschichte der exacten Wissenschaften," von J. C. Poggendorff. Dritter Band (die Jahre 1858 bis 1883 umfassend). Herausgegeben von B. W. Feddersen und A. J. von Oettingen. Leipzig, 1897—98. Roy. 8vo.

This valuable addition to Poggendorff's well-known biographical dictionary is useful to chemists, inasmuch as it gives the titles of original papers by the principal chemists of the world published during the period specified.

Works in Preparation and Reports of Progress.

"A Subject- and Author-Index to the first twenty volumes of the *Journal of the American Chemical Society*" is being compiled by Mr. Sohon, who expects to complete the MS. in December, 1898.

"A First Supplement to the Select Bibliography of Chemistry, 1492—1897," by Henry Carrington Bolton, is now going through the press. It will form a volume of the *Smithsonian Miscellaneous Collections* of about 600 pages.

"A Second Supplement" to the same Bibliography, to contain chemical dissertations only, is well advanced, about 8000 titles being already in hand.

Dr. A. C. Langmuir reports the completion of his MS. "Index to the Literature of Zirconium."

Dr. C. H. Joüet reports the near completion of his "Index to the Literature of Thorium."

Mr. George Wagner reports progress on a "Bibliography of Oxygen."

The manuscript of an "Index to the Literature of Thallium, 1861—1896," by Miss Martha Doan, lately of Cornell University, was submitted to the Committee, through Prof. L. M. Dennis, and after critical examination it has been unanimously recommended to the Smithsonian Institution for publication.

Dr. Alfred Tuckerman is engaged upon new editions of his "Indexes to the Literature of the Spectroscope, and of Thermodynamics," which are to be continued to the year 1900. He also reports progress on the "Index to the Mineral Waters of the World," the printing of which has been delayed by mechanical difficulties.

Dr. Willem P. Jorissen, of Rotterdam, has undertaken to bring down to date Prof. Albert R. Leeds' "Indexes to Ozone and to Hydrogen Peroxide," first issued in 1880, and long since out of print.

Monsieur Jules Garçon, chemical engineer (of 40 *bis* Rue Fabert, Paris), is about to publish an important contribution to the bibliography of technical chemistry, entitled "Répertoire Universel de Bibliographie des Industries Tinctoriales et des Industries Annexes." It is expected to form three large volumes. In the preparation of this immense undertaking the author has examined 1800 works and 111 sets of periodicals, the latter in 5000 volumes, besides 7000 other articles and documents. Subscriptions (100 francs) may be sent to the publishers, Gauthier-Villars et fils, Paris. M. Garçon is known as the author of the "Bibliographie de la Technologie Chimiques des Fibres Textiles," Paris, 1893, noted in our Thirteenth Annal Report.

Two unfinished manuscript indexes are at the disposal of persons willing to undertake their completion:—An "Index to the Literature of Carbonic Oxide," begun by the late Prof. William Ripley Nichols and continued by Prof. Augustus H. Gill; and an "Index to the Literature of Milk," begun by Prof. Clement W. Andrews.

As stated in previous reports, this Committee does not attempt to prescribe a fixed plan for volunteer indexers, but leaves method and topic to be chosen by compilers; the Committee does not seek to control the productions further than to insure work of high merit and to guard the interests of the Smithsonian Institution, which has agreed to publish manuscripts endorsed by the Committee. Chemists willing to undertake the compilation of indexes are requested to send their names and addresses, with a memorandum of the subject chosen, to the Chairman of the Committee (Cosmos Club, Washington, D. C.), who will furnish sample copies of indexes and other information.

Committee:—

H. Carrington Bolton, Chairman,
F. W. Clarke,
A. R. Leeds,
A. B. Prescott,
Alfred Tuckerman,
H. W. Wiley.

ESTIMATION OF TIN IN SALTS OF TIN.

By MM. A. FROENKEL and J. FASAL.

The authors have planned out a method for the estimation of tin which consists in precipitating this metal on aluminium, dissolving the two metals in hydrochloric acid, and titrating the stannous chloride thus formed by means of iodine or bichromate of potassium. But in this case it is indispensable to first of all neutralise nearly the whole of the hydrochloric acid. The method is as follows:—

The solution of the salt of tin containing 0·2 to 0·4 grms. of the metal is placed in a flask and a few drops of hydrochloric acid added, then from 0·5 to 1·0 grm. of aluminium wire. This is gently heated, and the tin is precipitated after about half an hour. At the end of this time 10 cubic centimetres of concentrated hydrochloric acid are added, and the whole warmed until the complete solution of both the metals has taken place; this requires about filteen minutes. Bicarbonate of soda and Seignette's salt are added until the reaction is alkaline. It is then titrated with iodine.

This method, tried with a solution (A) containing 0·4317 grms. of tin, and on another solution (B) containing 0·3988 grms of tin, gave the following results—

		A.	B.
1.	Tin found	0·4105	0·3866
2.	,,	0·4105	0·3875
3.	,,	0·4038	—

To find the difference between the quantity of tin actually existing in the solution and that found by analysis, we dissolved 2·8302 grms. of pure tin in hydrochloric acid, traversed by a current of carbonic acid. The volume of the solution was made up to 250 cubic centimetres, and 25 cubic centimetres of this solution were titrated in the manner already described. Another portion of 25 cubic centimetres was taken and oxidised, then precipitated either by sulphate of soda or by nitrate of ammonia; the oxide of tin was then weighed.

The following are the comparative results :—

Titration by iodine (1)	0·2765	grm.
,, ,, (2)	0·2767	,,
Titration by bichromate of potash	0·2736	,,
Precipitation by sulphate of soda ..	0·2870	,,
Precipitation by nitrate of ammonia	0·2844	,,

The theoretical result should be 0·2830 grm. of metallic tin.

The method is therefore a sufficient approximation for commercial purposes, and more especially in comparative analyses.—*Mitt. d. K. K. Tech. Gewerbe Museums in Wien*, vol. vii., p. 227.

ON THE ESTIMATION OF LEAD AND ANTIMONY IN TIN-FOIL.

By A. SEYDA.

Estimation of the Lead.—Ten grms. of the foil are dissolved in hydrochloric acid at 25 per cent, and a solution of nitric acid also at 25 per cent is added for the purpose of transforming the stannous chloride into stannic chloride, and to dissolve the antimony which remains unattacked by the hydrochloric acid. Drop by drop a solution of caustic soda at 25 per cent is added until the precipitate formed becomes re-dissolved. By maintaining the temperature at a point near boiling there is generally nothing but a slight opalescence left. We then add a small quantity of precipitated sulphur and treat with a current of sulphuretted hydrogen until the liquid takes a decidedly yellow tint. It is then allowed to stand for twenty-four hours, when the black precipitate is filtered off, washed with a solution of sulphide of sodium until a small portion of this clear liquid, acidulated with hydrochloric acid, gives a decidedly white deposit of sulphur. This washing requires a considerable time, but it is indispensable if we require the complete removal of the tin. The filter containing the moist precipitate is gently heated with nitric acid at 25 per cent, the solution is filtered, and the exhaustion with nitric acid repeated until a small portion of the filtered liquid no longer gives a black precipitate with sulphurretted hydrogen.

The nitric solution containing all the lead is evaporated down with 20 cubic centimetres of sulphuric acid. The sulphate of lead is filtered and weighed in the usual manner.

Estimation of the Antimony.—Five grms. of the tin-foil are thrown, a little at a time, into a mixture of 100 cubic centimetres of concentrated nitric acid and 25 cubic centimetres of water. The metastannic acid is treated with nitric acid at 25 per cent in a porcelain crucible and the mixture evaporated to dryness. The residue is dried on the water-bath. It is essential that the temperature of desiccation should not exceed 100° C., for the anhydrides of the oxides of tin and antimony do not appear to combine with soda. The still warm powder is thrown a little at a time into 60 grms. of caustic soda in a state of fusion. The melted mass is cooled to about 100°, broken up, and dissolved in 700 cubic centimetres of water. The cloudy liquid is cooled, and one-third of its volume of alcohol at 95 per cent is added, and the whole left for twenty-four hours. The precipitate is filtered by decantation, and the last portions washed on to a filter by means of a mixture of 1 part of water to 2 parts of alcohol. Instead of washing the precipitate with dilute alcohol, an operation which always removes a small portion of the antimony, it is better to repeat the fusion with caustic soda a second time. The precipitate is dried at 100° and separated from the filter. The latter is cut up into strips and thrown into 10 grms. of melted caustic soda containing a small quantity of nitrate of soda. When the paper is entirely consumed we add the precipitate and proceed as before.

To make quite sure of the insolubility of the antimoniate of soda, the liquid should contain about 10 per cent of caustic soda and 25 per cent of alcohol. The antimony is finally precipitated in the state of sulphide.—*Zeit. fur Offent. Chem.*, vol. iii., p. 364.

ON THE ELECTROLYTIC SEPARATION OF SILVER AND COPPER.

By N. REVAY.

These two metals may be separated one from the other by means of electrolysis, the silver salts requiring a slightly lower difference of potential than the corresponding salts of copper. The electrolysis can be effected either in acid solution or in a solution of double cyanides.

A. *Electrolytic Precipitation of Silver in Acid Solution.*—In the first experiment the electromotive force used was 1·3 to 1·4 volts. The silver was deposited in the spongy state; but this inconvenience can be avoided by heating the electrolyte to a temperature of 70° C.; the deposit of silver is even then not quite homogeneous, nevertheless it can be washed and weighed in this state. The electromotive force should not exceed 1·4 volt. To prevent the formation of peroxide, the solution should be kept strongly acid with nitric acid from the commencement of the reaction. The author has carried out experiments on solutions containing 0·25 to 0·50 grm. of nitrate of silver, and practically equal quantities of crystallised sulphate of copper. Four separate analyses showed that the nitrate of silver used contained 63·43, 63·47, 63·45, and 63·35 per cent of silver. These results may be looked upon as being very accurate.

B. *Electrolytic Precipitation in a Cyanide Solution.*—The separation based on this method was first suggested by Smith and Frankel. It was also experimented upon by Heydenrich and Frendenberg. In this case it is much more difficult to get a determined and constant electromotive force, as the difference of potential between the silver electrode and the solution varies considerably with the concentration of the silver salt and the proportion of cyanide of potassium in solution. According to Frendenberg the precipitation of the silver commences at 1·7 to 1·8 volts, while the copper is not deposited with an electromotive force lower than 2·3 to 2·4 volts; according to the present author, these last figures are a little too high. Experiments were made with an electromotive force of 1·6 to 1·8 volts at a temperature between 45° and 60°; the results obtained were very satisfactory. For six determinations made on electrolytes containing from 0·23 to 1·63 grms. of nitrate of silver he obtained 63·37 to 63·45 per cent of silver present in the salt used.

This method is preferable to the first one, inasmuch as it gives a more coherent metallic deposit. It gives better results still when the proportion of silver is high as compared with that of the copper present. On the other hand it is much less exact than the other method—to such an extent in fact, that if the copper is present in great excess it is precipitated the first.—*Zeitschrift fur Elecktrochemie*, vol. iv., p. 313, 1898.

THE ACTION OF SULPHUR UPON METALLIC SODIUM.

By JAMES LOCKE and ALFRED AUSTELL.

Among the various investigations which have been published regarding the action of sulphur upon metallic sodium but one is of recent date. Rosenfeld (*Ber. d. Chem. Ges.*, vol. xxiv., 1658), in a short article relating to the reactions of sodium, confirms the observations of Davy, Gay-Lussac, and Thenard, that the two combine with nearly explosive force, even at the ordinary temperature. Rosenfeld seems to have made no analysis of his reaction-products, but says that by mixing finely divided sodium, sulphur, and sodium chloride together, and rubbing, he obtained a violent reaction, in which a mixture of the monosulphide and polysulphides was formed. His work is accordingly given in the various reference books as indicating a method for preparing sodium monosulphide.

Through a chance observation made while preparing sodium sulphide in some other work, we have been led to study this reaction more closely. As it is practically impossible to separate the products from any sodium which may have been left unaltered in the reaction, a quantitative investigation of their composition is extremely difficult, and our results are therefore only approximate. They indicate conclusively, however, that the monosulphide cannot be formed by the direct combination of sodium and sulphur at temperatures below 220°.

Our method of procedure was as follows: A small weighed quantity of clean sodium was covered with about 50 c.c. of dry toluene, and the latter heated until the sodium fused. This was carried out in a small flask fitted with a return-condenser and a separatory-funnel. Through the latter the calculated quantity of sulphur, dissolved in hot toluene, was slowly added, while the contents of the flask were kept briskly boiling. The reaction at first results only in a thin yellow film of polysulphide* being formed upon the surface of the sodium. It soon grows violent, however; the sodium swells up, and a porous cake of the compound is formed. After this main reaction, which lasts but a few seconds, has subsided, the rest of the sulphur solution was added rapidly, and the mixture boiled for about an hour. The product was then filtered, washed with hot toluene, dried, and tested for sodium. The presence of uncombined sulphur in the mother-liquid could readily be seen from the yellow colour of the latter. When no free sodium was found, the substance was submitted to analysis.

Experiments were made successively with 2 grms. of sodium and the quantities of sulphur calculated for the compounds Na_2S, Na_2S_2, Na_2S_3, Na_2S_4, and Na_2S_5. The results are tabulated below:—

Ratios. Na : S.	Sodium. Grms.	Sulphur. Grms.	Product.	Filtrate.
2 : 1	2·0	1·39	Yellow, mixed with much Na	Colourless
2 : 2	,,	2·78	,,	,,
2 : 3	,,	4·17	Traces of Na	,,
2 : 4	,,	5·56	No Na	Yellow
2 : 5	,,	6·95	,,	,,

According to these results the only compound formed at 110°, the boiling-point of toluene, should approximate rather closely to the formula Na_2S_3. That no lower sulphide is formed is clear, and at this temperature metallic sodium has apparently no action upon the polysulphides. In the first two experiments, as the toluene cooled down, the globules of sodium left showed in fact a bright metallic lustre. The products of the last two experiments, in which there was no residual sodium, were analysed by conversion into the sulphate. They had practically the same composition with 28·89 and 28·57 per cent sodium respectively. The percentage of sodium calculated for the compound Na_2S_3 is 32·32, and for Na_2S_4 26·44. Both products were therefore probably mixtures of these two compounds. That more or less of the higher sulphide is formed is also indicated by the fact that the product obtained in the third experiment (Na : S = 2 : 3) contained a small quantity of free sodium.

An experiment was also made in which naphthalene was substituted for toluene, a temperature of 218° being thus obtained. It seemed probable that at this heat a compound containing less sulphur would be formed, if only by the action of sodium upon the polysulphides after the first reaction had taken place. This turned out, however, not to be the case. 2·78 grms. sulphur were dissolved in toluene, and added to 2 grms. sodium under hot naphthalene. The small quantity of toluene was then distilled off, and the naphthalene kept boiling for an hour. The product contained apparently as much free sodium as that obtained with a mixture of the same proportions at 110°.—*American Chemical Journal*, xx., No 7.

THE

CONDUCTIVITY OF AQUEOUS SOLUTIONS OF PRASEODYMIUM AND OF NEODYMIUM SULPHATES.

By H. C. JONES and H. M. REESE.

THE salts used in this work were those which had been employed by one of us (*Am. Chem. Journ.*, xx., 345), in determining the atomic weights of praseodymium and of neodymium. The partly purified compounds were kindly furnished by Mr. Waldron Shapleigh. These were further purified by the method described in the article already cited, and, as there shown, the amount of impurities which remained in the compounds must have been small.

The solutions of the sulphates, which had been made from the oxides, in determining the atomic weights of the metals, were evaporated to dryness, and heated above the boiling-point of sulphuric acid, until constant weight was attained. The salts was then allowed to cool, in weighing-tubes with ground-glass stoppers, and from these sulphates the following solutions were prepared.

The water used had been purified from ordinary distilled water, by the method described by Jones and Mackay (*Ibid.*, xix., 91), and was found to have an inappreciable conductivity.

In order to avoid the accumulative error which results from diluting a solution a large number of times, this was not repeated very often. A part of the original solution was diluted three or four times in succession, by removing a known volume from it, and adding a measured volume of water. The next dilution was prepared directly from the original solution, in a measuring-flask. This solution was then used as the starting-point in making the following three or four dilutions. The next more dilute solution was made directly from the original solution, and so on.

The Kohlrausch conductivity method, with Ostwald thermostat, was employed, and the cell standarised as usual with N/50 potassium chloride, which had been very carefully purified.

A solution of praseodymium sulphate was prepared containing 7·737 grms. in 200 c.c., which was equivalent to 38·685 grms. to the litre. The molecular weight of praseodymium sulphate was taken as 569·1; hence the above solution was 0·06798 normal, or its volume was 14·71. From this solution all the more dilute solutions of this salt were prepared as already described.

The solution of neodymium sulphate which was prepared contained 11·3595 grms. in 500 c.c. or 22·7190 grms. in a litre. The molecular weight of neodymium sulphate was taken as 575·4, the volume of the above solution being then 25·326. From this all the more dilute solutions were made.

The dilutions used, and the molecular conductivities found, for both salts, are given in the following table. v is the volume, or the number of litres which contains a grm.-molecular weight of the salt, and μ_v the molecular conductivities.

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* The fact that the film is yellow shows that even when a great excess of sodium is present no monosulphide forms, as the latter has a red colour. In every experiment made, a greenish-yellow product was obtained.

	Praseodymium sulphate.		Neodymium sulphate.	
	v.	μv.	v.	μv.
1	14·71	98·33	25·33	115·03
2	29·42	117·43	50·65	137·6 5
3	58·84	141·42	101·31	166·35
4	117·68	169·47	202·61	197·91
5	294·2	217 83	506·5	255·43
6	588·4	262·65	1013·0	303·45
7	1176·8	317·10	2026·0	366·0
8	1471·0	331·43	2532 6	382·9
9	2942·0	403·37	5065·2	462·5
10	5884·0	482·61		

—*American Chemical Journal*, xx., No. 7.

THE ATOMIC WEIGHT OF CADMIUM.*

By H. N. MORSE and H. B. ARBUCKLE.

HAVING re-determined the atomic weight of zinc (*Amer. Chem. Journ.*, xx., 195) by the method of Morse and Burton (*Ibid.*, x., 311), making corrections for the gas which Richards and Rogers (*Proc. Am. Acad.*, xxviii., 200) found to be retained by the oxide, even at high temperatures, we undertook a similar repetition of the work of Morse and Jones (*Amer. Chem. Journ.*, xiv., 261) on the atomic weight of cadmium, for the purpose of correcting their results, if cadmium oxide should also be found to retain gas.

Richards and Rogers found no gas in their specimens of cadmium oxide, but as their material had been heated to a higher temperature than is permissible in an atomic weight determination of this metal, we could not be certain that the oxide of Morse and Jones was likewise free from gas. Moreover, it was found by Bucher ("Dissertation," 1894, p. 22), in this laboratory, that when a given weight of cadmium oxide, derived from the carbonate, is converted into nitrate, and then again into oxide, the last weight of the oxide is greater than the first. The experience of Bucher points directly to the presence of gas in the oxide from the nitrate.

Another sufficient reason for a revision of the work is to be found in the fact that the results which have been obtained by work upon the halogen salts of cadmium have been throughout notably higher than those based on the weight of the oxide. It appeared desirable to clear up, if possible, the cause of this discrepancy between the two methods.

The metal which was used in this work was the same as that employed by Morse and Jones. It was, in fact, a portion of that prepared for the earlier experiments. It had been purified by six fractional re-distillations in a vacuum, and examined spectroscopically by Professor Rowland. The details of the distillation process have already been described (*Amer. Chem. Journ.*, x., 311, and xiv., 261) need not be repeated.

The nitric acid with which the metal was dissolved was prepared, as in the earlier work upon zinc and cadmium, by condensing the vapours of the acid upon the surface of a large platinum dish: 15 c.c. portions of it, when evaporated in platinum, gave no visible or weighable residue. We deemed it necessary to test the latter condition with unusual care, because of the wide difference between the atomic weights of cadmium and oxygen, and the correspondingly large effect of small errors in weight of material upon the results.

The arrangement of the crucibles in which the metal was converted first into nitrate, then into oxide, and finally weighed, was the same as that formerly used for both cadmium and zinc. It consisted of a small porcelain crucible (No. 00) in which the metal was dissolved, and a larger one (No. II.) in which the smaller one was placed. The smaller, but not the larger, crucible was provided with a lid. The lid and the crucible were, however, separated by means of bent pieces of platinum wire hung over the edge of the latter, thus providing for the free escape of vapours during the solution of the metal and the conversion of the nitrate into the oxide. The glaze was removed from the bottoms of the crucibles, also from the underside of the lid, by means of hydrofluoric acid. The pair of crucibles was weighed together and never separated. A similar, but slightly lighter, pair of crucibles was prepared at the same time to serve as a counterpoise. The platinum hooks belonging to the two sets were brought to nearly equal weight by filing, and then fragments of porcelain were added to the counterpoise until the weights of the two pairs differed by only a small fraction of a m.grm. Both were then heated under the same conditions for several hours. The difference between their weights was then carefully determined, after which they were again heated, in order to determine whether the difference remained constant. Throughout the entire determination the two sets of crucibles were treated as nearly alike as the purposes for which they were used would permit; for instance, if the pair in which the metal had been dissolved was heated, the tare was heated under the same conditions for the same length of time.

Owing to the volatility of cadmium oxide at high temperatures, it was necessary to give careful attention to our heating arrangements. A small double-walled furnace was made of asbestos board. Two opposite sides were cut away near their centres to permit the entrance of blast-flames, and the upper edges were notched to allow the products of combustion to escape. The bath, in which the crucibles previously described were heated, consisted of a large porcelain crucible. This was inserted in a hole in the piece of asbestos board which served as a cover to the furnace. In the bottom of the bath was placed a piece of unglazed porcelain on which the crucibles rested while being heated.

For the air-blast we had a small Root blower which was run by an electric motor; and, as the current was very constant, we were able to maintain quite uniform temperatures. The lamps which we first tried were two glass-blower's lamps with two jets each. These, with a given adjustment of air and gas-cocks, and speed of the blower, gave us a temperature in the furnace which lay between the fusing-points of sodium chloride (776°) and potassium carbonate (835°). As the former salt fused very readily, while the latter showed no signs of having been softened, we judge that the temperature must have been about 800°. At this temperature it was found practicable to reduce the oxide to constant weight. To ascertain whether a higher temperature might not be employed with safety, we substituted ordinary blast-lamps for those first selected. These gave us a temperature between the fusing-points of pure silver (960°) and potassium sulphate (1066°). But it was found that, at this temperature, specimens of oxide which had been brought to constant weight under the first arrangement began to lose in weight. That the loss was due, in part at least, to sublimation was clear from the fact that portions of the crucible previously white became tarnished with a yellow coating. The blast-lamps were therefore exchanged for those we had used in the first place, and no further change of lamps, or of gas or blast adjustments, was made during the entire work. The temperature was, however, tested from time to time, but always with the same result; sodium chloride fused readily, while potassium carbonate remained unfused, after heating for an entire day.

The apparatus for the liberation, collection, and analysis of the occluded gases was that devised for our earlier work on the atomic weight of zinc (*Amer. Chem. Journ.*, xx., 196). The manipulation of the specimens of oxide and of the gases was also the same as on the former occasion. We stated in our account of the work upon zinc that, in our judgment, the necessary errors connected

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* The work of which an account is given in this article was carried out under a grant from the Bache Fund (National Academy of Sciences).

with the gas analytical part of the determinations could not exceed 1 per cent of the correction. To test the reasonableness of this estimate, we made determinations of oxygen in three specimens of air whose volumes varied between 0·4 and 0·5 c.c. The percentages of oxygen found were 20·79, 20·98, and 20·80.

According to C. Langer and V. Meyer (*Pyrochemische Untersuchungen*, Seite 66) nitric oxide is not at all dissociated at temperatures between 900° and 1200°. Emich (*Monatshefte fur Chemie*, xiii., 615), on the other hand, states that the dissociation begins at 700°, is small at 900°, is only two-thirds completed at 1200°, and is not finished until the fusing temperature of platinum is reached. The results of both investigations indicate that the temperature of initial dissociation is higher, and its progress slower, than had hitherto been supposed. In view of the fact, therefore, that our oxide was never heated much above 800°, we had to fear the presence in it of oxides of nitrogen, a condition which would have increased very greatly the difficulty of the problem in hand. The following method of testing for the presence of nitric oxide, or other oxides of nitrogen, was adopted:—A wide-mouthed salt bottle was moistened on the inside with water; a crucible containing a quantity of cadmium oxide which had been heated to constant weight was introduced; a small quantity of dilute sulphuric acid, free from nitric acid, was added to the oxide, and the bottle closed. After standing for several hours, the liquid within was tested for nitric acid by the brucine reaction. None was found. In the subsequent work, the acid in which a specimen of oxide had been dissolved was examined, in every case, by means of the brucine reaction. In no instance, however, was any evidence of the presence of nitric acid found. In view of the fact that about 20 per cent of the gas retained by the oxide proved to be free oxygen, we judged that an examination of the solution, in the manner indicated, was sufficient to demonstrate the presence or absence of nitric oxide or other oxides of nitrogen.

Having converted the dried nitrate into a uniformly dark brown mass, at low temperature, the crucibles were placed in the furnace, previously described, and heated for a period of five or six hours. The tare was then heated for the same length of time, and the weight of the oxide determined. This operation was repeated, without variation, from five to eight times, until no change in the weight of the oxide could be detected after three successive heatings. The crucibles containing the oxide were then brought into our apparatus for dealing with the occluded gases, and there the oxide was treated in the same manner as the oxide of zinc in our earlier work (*Amer. Chem. Journ.*, xx., 195).

When the oxide of zinc is dissolved in dilute sulphuric acid, the evolution of the gas is slow, and continues as long as any of the material remains undissolved. In the case of the oxide of cadmium, on the other hand, a very different phenomenon presents itself. The instant the dilute acid strikes the oxide in the vacuum, there is an almost explosive evolution of gas; and though the solution of the oxide requires some time, but little gas is obtained after the instant of first contact between acid and oxide. The water vapour in the space above the crucibles condenses to a visible mist which settles upon the interior glass surfaces. The disturbance in the oxide, during this sudden liberation of gas, is so great that we were obliged to take measures to prevent it from being thrown out of the crucibles. The gas was collected and analysed in precisely the same manner as that obtained from the oxide of zinc.

The results of the nine determinations which were made are presented in the accompanying Table.

The uncorrected result, 112·084, is very close to the value 112·071 (112·06 with all corrections applied to weighings) which was obtained by Morse and Jones (*Amer. Chem. Journ.*, xiv., 264); while the corrected result, 112,377, accords equally well with the mean values 112·39 and 112·38, which were obtained by Bucher ("Dissertation," pp. 11 to 18), in his work upon the chloride and bromide of cadmium.

	Weight of cadmium.	Weight of oxide.	Uncorrected atomic weight.	Volume of gas (st. cond.). C.c.	P.cent. of oxygen.	Corrected atomic weight.
1	1·93188	2·20764	112·092	0·574	21·25	112·392
2	1·67935	1·91910	112·074	0·480	25·16	112·365
3	1·48430	1·69620	112·076	0·441	19·95	112·376
4	1·36486	1·55972	112·071	0·402	18·33	112·368
5	1·50295	1·71744	112·112	0·419	21·95	112·394
6	1·43804	1·64330	112·093	0·431	18·56	112·395
7	1·44041	1·64604	112·079	0·406	20·93	112·365
8	1·45938	1·66771	112·082	0·421	21·85	112·375
9	1·40379	1·60420	112·076	0·390	19·50	112·359
		Mean =	112·084		Mean =	112·377

The relation of the volume of the occluded gas to the weight of the oxide is remarkably constant, as will be seen from the following Table, in which is given for the individual determinations the volume of gas per grm. of oxide:—

	C.c.		C.c.		C.c.
1	0·260	4	0·258	7	0·246
2	0·250	5	0·244	8	0·252
3	0·260	6	0·262	9	0·243

The mean volume of the gas per grm. of the oxide is 0·253 c.c. as against 0·301 for the oxide of zinc.

A few experiments were made in order to determine whether the gas could be extracted without dissolving the oxide. The first of these was to ascertain whether the oxide, under water, would lose any portion of its gas when left for a long time in a vacuum. The bulb containing the acid was emptied and thoroughly washed with pure water, and then filled with water of perfectly neutral reaction. The water in the bulb was exhausted by occasional pumping until no trace of air could be obtained from it. A specimen of the oxide which had been heated for the usual length of time was then brought into the apparatus and covered with water. After exhausting again as completely as possible, connection with the pump was cut off and the oxide allowed to stand undisturbed for three days in the vacuum. Not a trace of gas was liberated. The next experiment was to determine whether boiling water would liberate the gas. A specimen of the oxide, weighing 1·4134 grms., which had been heated the usual length of time, but not tested as to the constancy of its weight, was heated for six hours under boilng water, and then dissolved in a vacuum. The volume of gas obtained was 0·403 c.c., or 0·284 c.c. per grm. of the oxide. It appears, therefore, that the oxide of cadmium does not lose its gas, either under water in a vacuum or under boiling water at atmospheric pressure.

Two experiments were made to determine whether oxide of cadmium still retains gas when heated to a temperature at which it begins to volatilise. The oxide was reduced to constant weight, and then, by substituting common blast-lamps for those ordinarily used, the temperature of the furnace was raised to a point lying between the fusing temperatures of pure silver (960°) and potassium sulphate (1066°). At this temperature the oxide lost in weight, very slowly, but nevertheless steadily; and the white porcelain of the crucibles became tarnished with a yellow coating, proving unmistakably that sublimation had begun.

Both samples of the oxide were four times re-heated, each time for six hours, and weighed after each heating. The separate losses were very minute; and, altogether, they amounted only to 1 m.grm. in one case and to 0·57 m.grm. in the other, showing that we had not exceeded the temperature of initial volatilisation. When these specimens of oxide were afterwards dissolved in a vacuum, one of them gave 0·240 c.c. and the other 0·247 c.c. of gas per grm. of oxide.

The gas from the oxide of cadmium was examined spectroscopically, after removal of the oxygen, and found to be nitrogen.—*American Chemical Journal*, xx., No. 7, July, 1898.

SOME PRINCIPLES AND METHODS OF ANALYSIS APPLIED TO SILICATE ROCKS.*

By W. F. HILLEBRAND.

(Continued from p. 94).

Zirconium.

This element is rarely looked for by chemists, though shown by the microscope to be one of the most constant rock constituents, usually in the form of zircon, in which occurrence its amount can be approximately judged of and a chemical test rendered almost unnecessary; but sometimes it occurs in other minerals, and is then unrecognisable under the microscope. It may rarely be presented up to a few tenths of 1 per cent of the rock.

For its detection and estimation in such cases, or whenever a search for it seems called for, the following procedure has been devised, which serves when carried out with care, to detect with certainty the merest trace—0·02 per cent, for instance—in 1 grm.

The powder is thoroughly fused with sodium carbonate, leached with water, the residue dissolved in a little hot dilute sulphuric acid, and filtered through the original filter, which is ignited, evaporated with hydrofluoric and sulphuric acids, and its solution added to the main one after filtration from any barium sulphate that may appear. To the solution, which should be in a small flask and contain not much above 1 per cent of pure sulphuric acid, is now added hydrogen peroxide to oxidise the titanium, and then a few drops of a soluble orthophosphate solution. The flask is then set aside in the cold for twenty-four to forty-eight hours. If the colour bleaches after a time, more hydrogen peroxide should be added. Under these circumstances the zirconium is thrown out as phosphate and collects as a flocculent precipitate, which, at this stage is not always pure. No matter how small or insignificant, it is collected on a filter, ignited, fused with sodium carbonate, leached with water, the filter again ignited, fused with very little acid potassium sulphate, brought into solution in hot water with a few drops of dilute sulphuric acid, poured into a flask of about 20 c.c. capacity, a few drops of hydrogen peroxide and of sodium phosphate added, and the flask set aside. Titanium is now almost never present, and the zirconium appears after a time as a white flocculent precipitate, which can be collected and weighed as phosphate. For the small amounts usually met with it is safe to assume that it contains 50 per cent of ZrO_2 (51·8 by theory). If the amount is rather large, it may be fused with sodium carbonate, leached, ignited, fused with acid potassium sulphate, reprecipitated by ammonia, and weighed as ZrO_2. Certainty as to its identity can be had by again bringing it into solution, precipitating by ammonia, dissolving in hydrochloric acid, evaporating to a drop or two, and testing with turmeric paper. With the very smallest amounts no colour can be obtained by the turmeric paper test, which, however, is readily available for as little as 1 milligrm, ZrO_2, and with the proper care for as small an amount as 0·3 milligrm. (Dr. H. N. Stokes). No element other than thorium is ever likely to contaminate the ZrO_2 thus precipitated.

This separation of zirconium from titanium in presence of hydrogen peroxide is founded on a method by G. H. Bailey (*Journ. Chem. Soc.*, vol. xlix., pp. 149, 481, 1886), but in his experiments the precipitation was not made by addition of a phosphate, but is said to be due solely to the hydrogen peroxide, the precipitate being a hydrated peroxide, Zr_2O_5 or ZrO_3 (Bailey, Chemical News, vol. lx., p. 6, 1889). My own efforts to secure a precipitate in acid solutions of zirconium sulphate by hydrogen peroxide alone were unsuccessful, perhaps for lack of a sufficiently strong peroxide. The ability to obtain the zirconium free from phosphoric acid would certainly be a great improvement on the method described above.

Were it not for the necessity of working in a much too acid solution, the separation of zirconium could be made in the same portion in which the titanium is colorimetrically determined.

Davis (*Am. Chem. Journ.*, vol. xi., p. 27, 1889), separates zirconium sharply from aluminum, but not from iron, by precipitation as an oxyiodate in a boiling neutralised solution of chlorides, but the method is hardly applicable for rock analysis.

Baskerville (*Journ. Am. Chem. Soc.*, vol. xvi., p. 475, 1894; Chemical News, vol. lxx., p. 57, 1894), has proposed a method for the separation of zirconium from iron and aluminum similar to his method for the separation of titanium from those elements (see *ante*). It is based on the precipitability of ZrO_2 by boiling the neutralised chloride solution for two minutes in presence of sulphurous acid, and seems to be excellent. As titanium is always present and is presumably quantitatively thrown down also, the two would have to be separated by hydrogen peroxide. No tests as to the availability of the method for separating the small amounts met with in rock analysis have been made.

Rare Earths other than Zirconia.

For the few cases in which it may be necessary to look for rare earths other than zirconia, the following procedure is suggested as likely to prove satisfactory in many cases:—

The rock powder is thoroughly decomposed by several partial evaporations with hydrofluoric acid, the fluorides of all earth metals except zirconium are collected on a platinum cone, washed with water acidulated by hydrofluoric acid, and the precipitate washed back into the dish or crucible and evaporated with enough sulphuric acid to expel all fluorine. The filter is burned and added. By careful heating the excess of sulphuric acid is removed and the sulphates are taken up by dilute hydrochloric acid. The rare earths, with perhaps some alumina, are then separated by ammonia, washed, re-dissolved in hydrochloric acid, and evaporated to dryness, then taken up with water and a drop of hydrochloric acid, and only enough ammonium acetate to neutralise the latter acid, followed by oxalic acid. In this way as little as 0·03 per cent of rare earths have been found when working on not more than 2 grms. of materials.

This method eliminates at once most of the aluminum, the iron, phosphorus, titanium, and zirconium, and has the further advantage of collecting with the earthy fluorides as UF_4 any uranous uranium that the rock might have held.

An alternative method would be to fuse with sodium carbonate, leach with water to get rid of phosphorus as far as possible, dissolve the residue in hydrochloric acid, separate silica as usual, precipitate alumina, &c., by ammonia, dissolve the precipitate again in hydrochloric acid, evaporate, and proceed as by the former method, which in most cases would undoubtedly give better results than this one.

Chromium, Phosphorus.

Silica is removed by hydrofluoric and sulphuric acids, excess of fluorine expelled, the residue brought into solution as far as possible with hydrochloric acid and hot water, filtered, the residue ignited, fused with sodium carbonate dissolved in hydrochloric acid, and the solution added to the main one, which is now precipitated by ammonia to get rid of the magnesium salts usually present

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* From the *Bulletin of the United States Geological Survey*' No. 148, p. 15, 1897.

and thus insure a cleaner subsequent fusion with sodium carbonate.

Separation of Alumina and Phosphoric Acid.—The precipitated Al_2O_3, P_2O_5, Cr_2O_3, Fe_2O_3, and TiO_2 is dissolved in hot hydrochloric acid and filtered into a large platinum crucible, the filter burned and added, the solution evaporated to pastiness, a little water added to dissolve the salts, and dry sodium carbonate added in portions and stirred in thoroughly to prevent lumpiness in the fusion to follow, which is continued for half an hour. Addition of sodium nitrate is not necessary. The melt is boiled out with water, and to the filtrate containing all the chromium and phosphoric acid and most of the aluminum ammonium nitrate is added till no further precipitation ensues. All P_2O_5 is thus removed, but not quite all alumina. After decanting, the precipitate is washed with ammonium nitrate solution, dissolved in nitric acid, and the phosphoric acid thrown out by molybdate solution.

Chromium.—The previous filtrate is acidified, boiled, rendered ammoniacal, and hydrogen sulphide introduced or fresh ammonium sulphide added. The precipitate of alumina and chromic oxide is now treated according to Baubigny (*Bull. Soc. Chimique*, N.S., vol. xlii., p. 291, 1884; Chemical News, vol. l., p. 18, 1885), by dissolving in hot nitric acid, evaporating to near dryness, and heating with strong nitric acid and potassium chlorate, then evaporating to dryness to get rid of the acid. On dilution with cold water, acid sodium carbonate is added in slight excess, and after two or three hours the precipitated alumina is filtered off. From the filtrate the chromium is then thrown out by fresh ammonium sulphide, redissolved to remove alkali, re-precipitated, and weighed.

Probably the separation of aluminum from chromium by hydrogen peroxide in ammoniacal solution, as recommended by Jannasch and Cloedt (*Zeitschr. fur. Anorg. Chemie*, vol. x., p. 402, 1895), would be preferable to the above if one has specially prepared hydrogen peroxide. The commercial brands are so impure that it is unsafe to employ them in most separations.

The above outline is from a paper by Dr. Chatard (*Am. Chem. Journ.*, vol. xiii., p. 106, 1891; *Bull. U.S. Geol. Survey*, No. 78, p. 87; Chemical News, vol. lxiii., p. 267, 1891), detailing a procedure devised in this laboratory for "the separation of titanium, chromium, aluminum, iron, barium, and phosphoric acid in rock analyses." If necessary, titanium, iron, and barium can be determined in the same portion, the reader being referred to the original paper for details.

Phosphorus in Rocks free from Chromium.—If the rock contains no chromium the phosphorus is determined as follows:—Fuse with sodium carbonate, dissolve in nitric acid, evaporate to dryness, take up with nitric acid, filter, ignite filter and treat with hydrofluoric and a drop of sulphuric acid, bring the small residue into solution by boiling with nitric acid and to the main portion, in which, after addition of ammonium nitrate, precipitate by ammonium molybdate solution. The turbidity often observed on dissolving the precipitated phosphomolybdate in ammonia is due to a compound of phosphorus which should always be re-fused with sodium carbonate and treated as above, in order to recover the phosphorus in it, if the addition of a small fragment of a crystal of citric or tartaric acid fails to dissolve it.

It is sometimes possible to extract all phosphorus from a rock by simple digestion with nitric acid; but quite as often, if not more often, this fails, and hence the necessity for resorting to the longer method.

Ferrous Iron.

Comparison of Sealed-tube and Hydrofluoric-acid Methods.—No point in rock analysis has been the cause of greater solicitude to the chemist, and especially to the mineralogist and petrographer, than the determination of iron in ferrous condition. The sealed-tube method with sulphuric acid, for a long time the only available one, is in theory perfect, since complete exclusion of oxygen is easily attainable. Its chief defect, however, lies in the inability to always secure complete decomposition of the iron-bearing minerals, and even to ascertain, oftentimes, whether or not the decomposition has been complete. The addition of hydrofluoric acid to the sulphuric in the tube, in order to insure this breaking up, is to be regarded as of very doubtful utility in most cases, since the glass may be so strongly attacked as to add an appreciable amount of iron to the solution, and the hydrofluoric acid may have exhausted itself in attacking the glass before the more refractory minerals succumb. Nevertheless, if decomposition can be effected by sulphuric acid alone the results obtained are sharp and concordant, and what is especially remarkable, and up to the present without a satisfactory explanation, they are in rock analyses invariably higher than when made by any of the modifications of the hydrofluoric-acid method now so extensively practised. This difference is not very marked with rocks containing but 1 or 2 per cent of the ferrous iron, but it increases with rising percentage to such an extent that where the sealed-tube method will show 12 per cent FeO the other may indicate no more than 10 per cent. This is a fact of which the writer has long been cognisant, but it does not seem to be known to chemists or petrographers at large, and it is one well deserving of critical examination. Attempts have from time to time been made to get at a solution of the problem, but without effect. Experiments with soluble iron salts of known composition, like ferrous sulphate or ferrous ammonium sulphate, throw no light on the subject, for both methods give the same sharp and accurate results with them. It is only when a silicate is taken that the difference appears. In titrating for ferrous iron the well-known rapid bleaching of the first permanent colour—the supposed crucial test of complete oxidation—in hydrofluoric-acid solutions of silicates, even with sulphuric acid present, has been thought to be perhaps in some way connected therewith. This bleaching is so pronounced that several c.c. of permanganate solution may be gradually added after the first so-called permanent colouration, without its being possible to obtain a persistent colour; and yet in hydrofluoric-sulphuric solutions of ferrous salts free from silica the first colouration is persistent for a long time.

The question now arises, which of these methods gives the correct result? My own opinion is in favour of the sealed-tube method with sulphuric acid, simply for the reason that there seems no possible chance for obtaining too high results thereby. No suggestion ever advanced to account for their being too high seems tenable. It has been proved over and over again that the error is not due to iron from the glass or to impurities in the sulphuric acid; a reduction of sulphuric acid with corresponding oxidation of ferrous iron seems impossible; and yet, did it occur, the result could be in nowise affected, for the amount of permanganate needed would be the same.

Notwithstanding this predilection in favour of the tube method, the one in exclusive use in this laboratory is that by decomposition by means of hydrofluoric and sulphuric acids. The results obtained by it are at least comparable with those found by other workers, and the impossibility of being assured of complete decomposition in a sealed tube is sufficient to condemn that method for general use.

Cooke's Method of Decomposing by Hydrofluoric and Sulphuric Acids.—The specially ground powder, in a capacious crucible, is placed, after stirring up with dilute sulphuric acid, on a small water-bath of a single opening, and covered with a glass funnel which rests in a depression of the cover, into which water constantly drops from a tubulated bottle, thus securing a perfect water-joint and serving to keep the bath full. Through a small metal pipe carbonic acid gas flows into the bath above the surface of the water, and rising through orifices in the cover fills the funnel and crucible (J. P. Cooke, *Am. Jour. Sci.*, 2nd ser., xliv., p. 347, 1867). The lamp under the bath is lighted, and hydrofluoric acid is poured into the crucible through a platinum funnel, which is left in place to serve as an occasional stirrer, for which a rod or wire may be substituted. After boiling commences the rapid gas current can be safely interrupted, to be restored when the lamp is extinguished after one-half to one or more hours. A full stream of cold water is then caused to flow from the tubulated bottle into the bath, the overflow from the outlet tube being caught in a receiver. As soon as cool the contents of the crucible are emptied into a platinum dish containing cold water, and titrated till the first permanent colour appears, which usually will last for only a few seconds. Duplicate determinations are to be advised whenever possible, since even with the utmost care the results will occasionally differ more than is allowable.

Pratt's Modification of the Hydrofluoric-acid Method.—J. H. Pratt (*Am. Jour. Sci.*, 3rd ser., xlviii., p. 149, 1894) has shown that very satisfactory ferrous iron determinations can be secured by simple boiling of the rock powder with hydrofluoric and sulphuric acids in a large crucible fitted with a cover and platinum tube for introduction of carbon dioxide. His test experiments on ferrous sulphate show that there need be practically no oxidation, even if the heating lasts several hours. The directions given in his paper (p. 150), with reference to the treatment of very refractory minerals which are not fully decomposed by this treatment, must be understood as referring only to homogeneous minerals and not to rocks, where the relations of ferrous and ferric iron in the undecomposed portion are certainly different from those in the part dissolved.

Influence of Sulphides.—The presence of pyrite or marcasite is probably without serious effect on the ferrous-iron determination by any of the hydrofluoric-acid methods. These sulphides are very resistant toward attack in the absence of oxygen, as is shown by the fact that if present in any quantity they can be readily recognised in the residue after titration. In any case it is impossible to allow for an error introduced by their possible decomposition, and the result of titration must count as ferrous iron. In the case of soluble sulphides two sources of error are introduced—that of reduction of ferric iron by hydrogen sulphide evolved, and that due to the ferrous iron which the sulphides themselves may contain especially if pyrrhotite is present. The first of these is perhaps negligible, since most of the hydrogen sulphide would probably be expelled without reducing iron. The second is approximately measurable if it is known that pyrrhotite is the only soluble sulphide present and its amount has been ascertained by determining the hydrogen sulphide set free on boiling with hydrochloric acid in a current of carbon dioxide. In this case a correction is to be applied to the result of titration for total ferrous iron. (See also under Sulphur).

(To be continued).

CORRESPONDENCE.

THE KINETIC IMAGINING OF GASES.

To the Editor of the Chemical News.

Sir,—Mr. Emmens appears to be not well pleased with the review of the pamphlet "The Kinetic Imagining of Gases" which recently appeared in your journal, and seems desirous of discussing the matter further with me.

If this is his desire, I must decline to gratify him, for it does not appear to me that any good can result from arguing with a man who is not only ignorant of the fact (among others) that the earth rotates on its axis every year once more than the number of days in the year, but is so lacking in intelligence as to be unable to appreciate the fact when it is pointed out to him.—I am, &c.,

The Writer of the Review.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Berichte der Deutschen Chemischen Gesellschaft.

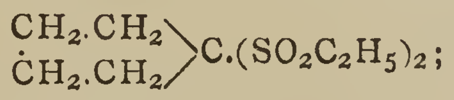
No. 4, 1898.

Action of Oxalic Diethyl Ethers on *p*-Amidophenol and its Ether.—A. Piulti and R. Piccoli.—When oxalic ether and *p*-amidophenol are heated at 160° for an hour in sealed tubes, a substance is formed, soluble in hot water and acetic acid, with melting-point 184—185°, which analysis proves to be *p*-oxyphenyloxamine,—

$$C_2H_5.OOC.CO.NH.C_6H_4.OH.$$

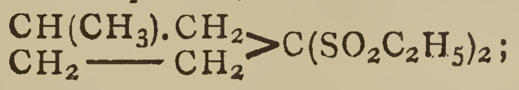
p-Methoxyphenyloxaminic ester, crystallising in long white needles and melting at 108—109°, is prepared by acting on *p*-anisidine with oxalic ester and extracting with hot water. *p*-Ethyloxyphenylaminic ester is formed when oxalic ester acts on *p*-phenetidine; it crystallises in bright hexagonal plates (m. p. 108—110°), which are soluble in hot water, alcohol, and acetic acid.

Sulphonated Cyclic Ketones.—O. Wallach and Walther Borsche.—The authors have prepared pentanone sulphonal,—



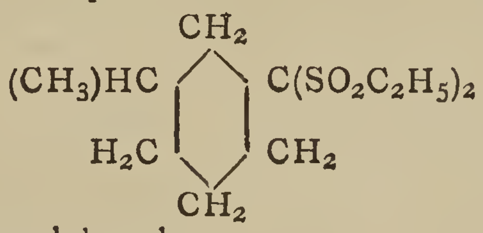
$$\left.\begin{matrix}CH_2.CH_2\\ \dot{C}H_2.CH_2\end{matrix}\right\rangle C.(SO_2C_2H_5)_2;$$

methylpentanone sulphonal,—

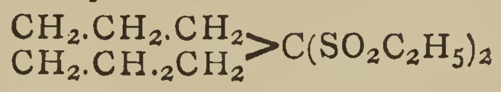


$$\left.\begin{matrix}CH(CH_3).CH_2\\ CH_2 \text{———} CH_2\end{matrix}\right> C(SO_2C_2H_5)_2;$$

methylhexanone sulphonal,—



and heptanone sulphonal,—



$$\left.\begin{matrix}CH_2.CH_2.CH_2\\ CH_2.CH._2CH_2\end{matrix}\right> C(SO_2C_2H_5)_2$$

by the action of mercaptan on the penta-, hexa-, and hepta-cyclic ketones.

Diazonium Hydrate in Aqueous Solution.—A. Hantzsch.—The author finds that the best method of preparing pure diazonium hydrate solution was by dissolving pure diazonium chloride in water, and shaking this up with the calculated quantity of silver oxide whilst keeping it cooled in ice. The solution is very unstable, being a clear bright yellow solution at 0°, but becoming reddish brown at ordinary temperatures with separation of a flocculent resin. With silver nitrate a brown precipitate is formed; with mercuric chloride, a precipitate soluble in excess.

Formation of Metallic Sodium from Sodium Peroxide.—Heinrich Bamberger.—The author prepares metallic sodium in the following ways:—(1). Na_2O_2 and charcoal are well powdered and heated in a crucible to 300—400°. The following reaction takes place:—$3Na_2O_2+2C=2Na_2CO_3+Na_2$. The reaction is violent, the sodium being found condensed on cooling on the lid and upper part of the crucible. (2). Na_2O_2 and CaC_2 are heated together, the reaction taking place with explosive violence according to the equation $7Na_2O_2+2CaC_2=2CaO+4Na_2CO_3+3Na_2$.

Action of Acetic Anhydride on the Anilides of Dibasic Acids.—H. v. Pechmann and Wilh. Schmitz.

Nitrogen Derivatives of Benzylacetophenones.—T. Tambor and F. Wildi.

Paradinitrodibenzyldisulphonic Acid.—C. Rio and C. Simon.

Some Esters and a Crystalline Pseudo-ester of Rhodinol.—Ernst Erdmann.

Investigations on Optic Activity.—L. Tchúgaeff.

The 3-Oxy-1 . 2 . 4-triazoles, and some Acidylsemicarbazides.—O. Widman and Astrid Cleve.

Action of Anilines on Dioxytartaric Acid.—Arnold Reissert.

Action of Oxalic Ester and Sodium Ethylate on Substituted Nitrotoluoles. — Arnold Reissert and J. Scherk.

Action of Oxalic Ester and Sodium Ethylate on Nitrocresolmethyl Ether $(OCH_3 : CH_3 : NO_2 = 1 : 3 : 6)$.—Arnold Reissert.

Derivatives of Cycloheptanes.—Eduard Buchner and Andreas Jacobi.

β-Isophenylacetic Acid. — Eduard Buchner and Ferdinand Lingg.

Choline and Trigonelline in the Seeds of Strophanthus kombé.—Hermann Thoms.

Alkyl-sulphonic Acid Salts.—Arthur Rosenheim and Otto Liebknecht.

Action of *o*-Xylylenbromide on Primary, Secondary, and Tertiary Amines.—M. Scholtz.

Synthesis of Xanthines from Hydrocyanic Acid.—Armand Gautier.

New Method of Molecular Weight Determination by the Boiling-point Method.—W. Landsberger.

Method of Formation of *p*-1-Nitrodiphenyltetrazols.—Edgar Wedekind.

Journal de Pharmacie et de Chimie,
Series 6, vol. vii., No. 10.

The Gelatinous Matter (Pectine) in Gentian Root.—MM. E. Bourquelot and H. Herissey.—Most pharmacopœias recommend maceration for the preparation of the aqueous extract of gentian, but there is a gelatinous body present which has no therapeutic properties, and which renders filtration difficult. It has been isolated by digesting for three quarters of an hour at from 80°—90° in water acidulated with hydrochloric acid; the clear liquid is then precipitated by alcohol at 90°. The jelly thus obtained is strained through fine muslin, washed with alcohol, then re-dissolved in water and again precipitated by alcohol; after a final washing with ether the product was dried between sheets of filter paper, and then in the air. The results of some experiments showed that there must be either some resinous body present in the gentian root which has the power of preventing its solution in water, or that pectose, susceptible during desiccation or trituration of being transformed from soluble pectine into insoluble pectic acid, is present. The authors eventually found that with a mineral acid, a very different product was obtained to that got by water only. It is possible in the first case to obtain a pectine mixed with hydrates of carbon strongly dextrogyre, separated by the acid from the cellular membrane.

Formulæ for the Rapid Estimation by Duclaux's Method of the Volatile Acid Products of a Fermentation.—MM. Bordas and De Raczkowski.—A purely mathematical paper not suitable for abstraction.

THE CHEMICAL NEWS.

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(STUDENTS' NUMBER).

ADDRESS TO STUDENTS.

It is once more our duty to indite a few remarks, intended more especially for those among our readers who are about to take one of the most important steps which will influence their future career. We chiefly address those Students who, having made choice of a profession, are, within the next few weeks, about to enter on the actual work of learning it. At school they have had, we hope, the necessary training to get "fit"—they have now to realise the necessity for work, and be it remembered that, in these days of advanced and rapidly expanding science, he who loses time at the beginning runs a great risk of being left behind in the race.

Specialism is the order of the day, and the sooner the Student finds out which particular branch of science is best suited to his taste and opportunities, the sooner will he be able to stand in line with the masters of that subject.

It must not be imagined that we are advising narrowness of study; on the contrary, the widest read man has the greatest aptitude for absorbing and digesting new ideas.

We cannot too strongly urge on every Student to make use of all his opportunities for acquiring knowledge, and, above all, never to forget that the final examination is *not* the be-all and end-all of the course of instruction he is about to enter upon.

As the cautious Alpine climber makes sure that one foot is firmly placed before he takes another step forward, still keeping the summit in view, so must the seeker after success make sure that his groundwork is solid; at school he learns how to learn, at College he learns, but in after life he has to find out and teach himself: this will be made easier if he remembers that, no matter how many competitors there are, there is always room on the top.

We cannot close these remarks without expressing our regret that the authorities at the War Office have decided to do away with part of the scientific training at the Royal Military College at Woolwich, by closing the chemical laboratory: this is decidedly a movement to the rear.

UNIVERSITIES AND COLLEGES.

UNIVERSITY OF LONDON.

Candidates for any Degree in this University must have passed the Matriculation Examination. No exemption from this rule is allowed on account of Degrees obtained or Examinations passed at any other University. This and all other Examinations of the University, together with the Prizes, Exhibitions, Scholarships, and Medals depending upon them, are open to Women upon exactly the same conditions as to Men.

There are two Examinations for Matriculation in each year; one commencing on the second Monday in January, and the other on the second Monday in June.

The Examination is conducted by means of Printed Papers; but the Examiners are not precluded from putting, for the purpose of ascertaining the competence of the candidates to pass, *viva voce* questions to any candidate in the subjects in which they are appointed to examine. These Examinations may be held not only at the University of London, but also, under special arrangement, in other parts of the United Kingdom, or in the Colonies.

Every candidate for the Matriculation Examination must, not less than five weeks before the commencement of the Examination, apply to the Registrar for a Form of Entry, which must be returned not less than four weeks before the commencement of the Examination, accompanied by a Certificate showing that the candidate has completed his sixteenth year, and by his Fee for the Examination. As no candidate can be admitted after the List is closed, any candidate who may not have received a Form of Entry within a week after applying for it must communicate immediately with the Registrar, stating the exact date of his application and the place where it was posted.

Every candidate entering for the Matriculation Examination for the first time must pay a Fee of £2 to the Registrar. If a candidate withdraws his name, or fails to present himself at the Examination, or fails to pass it, the Fee shall not be returned to him, but he shall be allowed to enter for any subsequent Matriculation Examination upon payment, at every such entry, of an additional Fee of £1, provided that he comply with the Regulations in the preceding paragraph.

Candidates are not approved by the Examiners unless they have shown a competent knowledge in each of the following subjects:—Latin. Any one of the following Languages:—Greek, French, German, Sanskrit, or Arabic. The English Language, and English History, with the Geography relating thereto. Mathematics. Mechanics. One of the following branches of Science:—Chemistry, Sound, Heat and Light, Magnetism and Electricity, Botany.

The Examination in Chemistry is—Chemistry of the Non-metallic Elements; including their compounds, their chief physical and chemical characters, their preparation, and their characteristic tests

A Pass Certificate, signed by the Registrar, will be delivered to each successful candidate after the Report of the Examiners has been approved by the Senate.

If in the opinion of the Examiners any candidates in the Honours Division of not more than twenty years of age at the commencement of the Examination possess sufficient merit, the first six among such candidates will receive an Exhibition of thirty pounds per annum for the next two years; the second among such candidates will receive an Exhibition of twenty pounds per annum for the next two years; and the third will receive an Exhibition of fifteen pounds per annum for the next two years; such exhibitions are payable in quarterly instalments provided that on receiving each instalment the Exhibitioner declares his intention of presenting himself either at the two Examinations for B.A., or at the two Examinations for B.Sc., or at the Intermediate Examination in Laws, or at the Preliminary Scientific M.B. Examination, and Intermediate Examination in Medicine, within three academical years from the time of his passing the Matriculation Examination.

Under the same circumstances, the fourth among such Candidates will receive a prize to the value of ten pounds in books, philosophical instruments, or money; and the fifth and sixth will each receive a prize to the value of five pounds in books, philosophical instruments, or money.

Any candidate who may obtain a place in the Honours Division at the Matriculation Examination in January is admissible to the Intermediate Examination either in Arts or in Science in the following July.

Intermediate Examination in Science.

The Intermediate Examination in Science will commence on the second Monday in July.

No candidate (with the exception of such as have obtained Honours at the Matriculation Examination in the preceding January) is admitted to this Examination within one academical year of the time of his passing the Matriculation Examination.

The Fee for this Examination is £5.

Examination for Honours.

Candidates for Honours in Chemistry will be examined in Inorganic Chemistry, treated more fully than in the Pass Examination. In addition, they will be examined practically in Simple Qualitative Analysis. This Examination will consist of six hours' examination by two printed papers and of six hours' practical work.

In the Examination for Honours, the Candidate, not being more than 22 years of age at the commencement of the Pass Examination, who most distinguishes himself will receive an Exhibition of £40 per annum for the next two years.

B.Sc. Examination.

The B.Sc. Examination will be held on the fourth Monday in October.

Candidates for this Examination are required to have passed the Intermediate Examination in Science at least one academical year previously.

The Fee for this Examination is £5.

Examination for Honours.

For the examination for Honours in Chemistry two papers will be set and a two days' practical examination.

The candidate, being not more than 23 years of age, who most distinguishes himself in Chemistry, will receive £50 per annum for the next two years, with the style of University Scholar.

Doctor of Science.

The examination for the Degree of Doctor of Science takes place annually within the first twenty-one days of June.

No candidate is admitted to the examination for the Degree of D.Sc. until after the expiration of two Academical Years from the time of his obtaining the Degree of B.Sc. in this University.

Every candidate for this Degree must state in writing the special subject within the purview of the Faculty of Science, as set out in the Programme of the B.Sc. Examination, upon a knowledge of which he rests his qualification for the Doctorate; and with the Form of Entry he shall transmit an original Dissertation or Thesis (at least six copies), printed, type-written, or published in his own name, treating scientifically some special portion of the subject so stated, embodying the result of independent research, or showing evidence of his own work, whether conducted independently or under advice, and whether based on the discovery of new facts observed by himself, or of new relations of facts observed by others, or, generally, tending to the advancement of Science. Every candidate may further specify any printed contribution or contributions to the advancement of Science which he has at any time previously published. If the Dissertation or Thesis be approved by the Examiners, the candidate shall be required to present himself at the University upon such day or days within the first twenty-one days of June as may be notified to him, and shall, at the discretion of the Examiners, be further tested, either orally or practically, or by printed questions or by all of these methods, with reference both to the special subject selected by him and to the Thesis.

Preliminary Scientific (M.B.) Examination.

This Examination takes place twice in each year,—once, for Pass and Honours, commencing on the second Monday in July; and once for Pass Candidates only, commencing on the third Monday in January.

No candidate shall be admitted to this Examination unless he shall have passed the Matriculation Examination. Not less than five weeks before the commencement of the Examination he must apply to the Registrar for a Form of Entry, which must be returned not less than four weeks before the Examiantion, accompanied with the candidate's fee.

The Fee for this examination is Five Pounds.

UNIVERSITY OF OXFORD.

Waynflete Professor of Chemistry—W. Odling, M.A., F.R.S.

Every Student must reside in one or other of the Colleges or Halls, or in licensed lodgings, for a period of three years. Students of Chemistry can obtain the degree of B.A. by passing preliminary examinations in Arts and in Science, and a final Honour examination in Chemistry. Chemistry may also be taken as part of the examination for a Pass degree. Graduates of other Universities suitably qualified can obtain the degree of Bachelor of Science after an approved course of study or research and two years' residence.

University Laboratory.—Demonstrators, W. W. Fisher, V. H. Veley, F.R.S., J. E. Marsh.—The fee for students working in the Laboratory for three days in the week during the Term is £3; for students working every day, £5.

Christ Church Laboratory.—A. Vernon Harcourt, F.R.S.

Scholarships of about the value of £80 are obtainable at the majority of the colleges, by competitive examination in Natural Science.

More detailed information may be obtained from the Examination Statutes; the Student's Handbook to the University; and from the professors and college tutors.

UNIVERSITY OF CAMBRIDGE.

Professor of Chemistry—G. D. Liveing, M.A., F.R.S.

Jacksonian Professor of Natural and Experimental Philosophy—J. Dewar, M.A., F.R.S.

The Student must enter at one of the Colleges or Hostels, or as a Non-collegiate Student, and keep terms for three years by residence in the University. He must pass the previous examination in Classics and Mathematics, which may be done in the first or third term of residence, or, through the Oxford and Cambridge Schools Examination Board, or through the Senior Local Examinations, before commencing residence. He may then proceed to take a Degree in Arts, either continuing mathematical and classical study, and passing the ordinary examinations for B.A., or going out in one of the Honour Triposes.

The scholarships, ranging in value from £20 to £100 a year, are chiefly given for mathematical and classical proficiency. Scholarships, or Exhibitions, are given for Natural Science in King's, Trinity, St. John's, St. Peter's, Clare, Trinity Hall, Queen's, Jesus, Christ's, Sidney, Pembroke, Caius, and Downing Colleges; the dates of the examinations vary, but are always fully advertised.

The Chemical Laboratory of the University is open daily for the use of the Students. The Demonstrators attend daily to give instructions. A list of the lectures is published annually, in June, in a special number of the *Cambridge University Reporter*, which may be had from the Cambridge Warehouse, in Paternoster Row, or through any bookseller.

Non-collegiate Students are allowed to attend certain of the College Lectures and all the Professors' Lectures, and have the same University status and privileges as the other Students. Full particulars may be obtained by forwarding a stamped directed envelope to the Assistant Registrar, Cambridge, or from the *Cambridge University Calendar*.

UNIVERSITY OF DUBLIN.

Trinity College.

Professor of Chemistry—J. Emerson Reynolds, D.Sc., M.D., F.R.S.

Assistant Lecturer—Emil A. Werner, F.C.S., F.I.C.

Demonstrator—J. Percy Bailey, B.A.

The general Laboratories include working accommodation for 120 Students, and the Quantitative and Research Laboratories for about 40 Students. The Laboratories will open on the 1st of October. Lectures will commence about November 1st.

The Laboratories and the Lectures ofthe Professor of Chemistry can now be attended by Students who do not desire to reside in the University or proceed to its Degrees, The full Course of General and Analytical Chemistry occupies three years, but a Student is free in his third year to devote most of his time to a special department of Pure or Technical Chemistry. Students can enter for any portion of the Course. The following Lectures are delivered:—

1. *Inorganic Chemistry and Chemical Philosophy.*—Elementary, first year; advanced, second year.
2. *Organic Chemistry.*—General, second year; advanced, third year.
3. *Metallurgy.*—A Course for Engineering and Technical Students.

The Laboratories are open every day from 10 to 5 o'clock (except Saturdays, when they close at 1 o'clock).

The Summer Course of Practical Chemistry for Medical Students begins during the first week in April and terminates with the first week in July.

The University of Dublin grants the Degree of Doctor of Science to graduates of Master's standing whose independent researches in any branch of Science are of sufficient merit.

KING'S COLLEGE.

(Division of Engineering, Architecture, and Applied Science).

Professor of Chemistry—J. M. Thomson, F.R.S., F.C.S.

Demonstrator of Practical Chemistry—Herbert Jackson, F.C.S.

Assistant Demonstrator—P. H. Kirkaldy, F.C.S.

The Academical Year consists of Three terms. The days fixed for the Admission of New Students in the Academical Year 1898-99 are October 4, January 18, and April 26.

Students of the First Year are admitted to the Course of Theoretical and Applied Chemistry. The Course commences with a view of the conditions suitable for the production of Chemical Phenomena, after which the laws of Chemical Attraction are discussed, and the Non-metallic Elements and their principal compounds are described. The Metals and their principal compounds are next examined, care being taken to point out the applications of the Science to the Arts; and the processes of the different Manufactures and of Domestic Economy are explained and illustrated. Examinations of the Class, both *vivâ voce* and by written papers, are held at intervals during the course at the usual Lecture hour.

Second Year.—Students attend in the Laboratory twice a week, and they go through a course of Manipulation in the most important operations of Chemistry, including the first steps of Analysis. Any Student of this Division may be admitted to this Class at any period of his study on payment of an extra fee.

Experimental and Analytical Chemistry in the Laboratory.—The object of this Class is to afford to Students who are desirous of acquiring a knowledge of analysis, or of prosecuting original research, an opportunity of doing so under the superintendence of the Professor and Demonstrator; Students may enter, upon payment of extra fees, at any time except during the vacation, and for a period of one, three, six, or nine months, as may best suit their convenience. The laboratory hours are from ten till four daily, except Saturday, on which day the hours are from ten till one.

In addition to the Laboratory Fee, each Student defrays the expenses of his own experiments. The amount of this expense, which is comparatively trifling, is entirely under his own control.

Special hours and fees are arranged for the convenience of such Third Year Students as wish to study Analytical Chemistry.

Fees.—Chemistry per term, £3 3s. od.; per ann., £8 8s. od.; Practical Chemistry per term, £4 4s. od.; per ann., £10 10s. od.; Experimental and Analytical Chemistry—Five days a week: One month, £4 4s.; Three months, £10 10s.; Six months, £18 18s.; Nine months, £26 5s. Three days a week: One month, £2 12s. 6d.; Three mos., £6 6s.; Six mos., £11 11s.; Nine mos., £15 15s.

Metallurgy.

Professor—A. K. Huntington, F.I.C., F.C.S., &c.

The following subjects are treated of in the Lectures: The Selection and Economic Preparation of Fuel and of Refractory Materials; the methods by which metals are obtained from their ores, and the means by which they are rendered suitable for the various requirements of the Arts.

Particular attention is paid to the study of the Nature and Properties of Metals and Alloys available for Constructive Purposes.

In the Metallurgical Laboratory, which is always open during College hours, the relation between the Chemical Composition of Metals and their Mechanical Properties may be studied by the aid of Testing Machinery.

Photography.

Lecturer—Prof. J. M. Thomson, F.R.S., F.C.S.

In addition to the regular College Course in Photography occasional classes may be formed. For further particulars application should be made to Prof. Thomson.

Evening Classes.

Classes for Evening Instruction in various subjects are held during the Winter Session.

UNIVERSITY COLLEGE.

Faculty of Science.

Professor—William Ramsay, LL.D., F.R.S.

Assistants—Morris Travers, D.Sc., Alexander Kellas, B.Sc., and E. C. C. Baly, F.I.C.

The Session is divided into three Terms, as follows, all the dates being inclusive:—

First Term, from Tuesday, October 4th, until Friday, December 16th;

Second Term, from Tuesday, January 10th, 1899, till Friday, March 24th;

Third Term, from Tuesday, April 18th, till Friday, June 30th. Class Examinations begin on June 19th.

Junior Courses of Inorganic Chemistry.

First Term: Tuesday, Thursday, and Saturday at 10. Latter half of Second and Third Term: Tuesday, Thursday, and Saturday. Fee:—£4 4s.

These Courses will each consist of about thirty lessons, partly theoretical and partly practical, on the non-metallic elements. Frequent exercises will be given.

Senior Course of Inorganic Chemistry.

First and Second Terms: The Class meets four times a week, on Mondays, Wednesdays, Fridays, and Saturdays, at 9, for Lectures, Examinations, and Exercises.

Fees:—For the Course, £7 7s.; Perpetual, £9 9s.; for the First or Second Terms, £4 4s.

This Course and the Practical Class cover the subject as prescribed for the Preliminary Scientific (M.B.) and Int. Examination in Science of the University of London.

For the Preliminary Scientific Examination Students who take the three subjects for that examination in July attend during the First and Second Terms.

Advanced Course of Chemistry.

Second and Third Terms.—The class meets twice a week, on Tuesdays and Thursdays, at 9, beginning on January 10. The hour will be altered by special arrangement with the class if necessary.

Fee:—For the Course, £3 3s.; for a Term, £2 2s.

This Course will be found suitable for those about to proceed to graduation as Bachelor of Science in London University, and to those who intend to choose Chemistry as a profession. Such students should also work in the Laboratory during as many hours as they can spare.

Organic Chemistry.

Tuesday, Thursday, and Saturday, at 9, in the First Term; Tuesday, Thursday, and Saturday, at 10, in the Second Term; and Tuesday and Thursday at 9, and Saturday at 11, in the Third Term. The hour of meeting will be altered should the class desire it.

This Course of Organic Chemistry is intended for those who are studying the subject from a scientific standpoint. Candidates for Honours at the Int.M.B. are, however, recommended to attend this Course besides the Special Summer Course.

The Course includes the subjects required at the B.Sc. Examination, Pass and Honours; but no previous acquaintance with Organic Chemistry will be expected of those joining the Class.

Fee:—For the Course, £6 6s.; for the Second and Third Terms, £4 14s. 6d.; for a Term, £2 12s. 6d.; for a Second Course, £3 3s.

Practical Classes.

Practical Classes in Inorganic and Organic Chemistry are conducted by the Assistants.

Analytical and Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., Saturdays excepted, from October until the middle of July, with a short recess at Christmas and at Easter.

Fees: for the Session, £26 5s.; six months, £18 18s.; three months, £10 10s.; one month, £4 4s.

Three specified days a week:—for the Session, £15 15s.; six months, £11 11s.; three months, £6 6s.; one month, £2 12s. 6d., exclusive of expense of materials. Students may enter at any period of the Session.

The Laboratory Course includes the Practical Chemistry required at the following Examinations of the University of London:—Prel. Sci. (M.B.), Intermediate M.B., Intermediate Science, B.Sc.

Students who wish to attend the Lectures on Chemical Technology may acquire here the requisite knowledge of Practical Chemistry and Analysis.

When accompanied by, or preceded by, attendance on the Lectures on Inorganic and Organic Chemistry, the Laboratory Course qualifies Students in the application of Chemistry to Manufactures, Metallurgy, Medicine, or Agriculture, &c.

There is also a Chemical Library containing the chief Journals and Standard Works on Chemistry.

Certificates of Honour are granted to competent Students on the work done during the Session. The Tuffnell Scholarship (£100 for two years) will also be competed for in the Session 1898-99; also the Clothworker's Scholarship of £30.

ROYAL COLLEGE OF SCIENCE AND ROYAL SCHOOL OF MINES.

Professor—W. A. Tilden, D.Sc., F.R.S.

Assistant Professor—W. P. Wynne, D.Sc., F.R.S.

Demonstrators—H. Chapman Jones and M. O. Forster, Ph.D.

Assistants—G. S. Newth and G. T. Morgan, B.Sc.

The Royal College of Science at South Kensington is intended, primarily, for the instruction of teachers, and of students of the industrial classes selected by competition in the examinations of the Science and Art Department. The Royal School of Mines is incorporated with the Royal College of Science. Students entering for the Associateship of the Royal School of Mines obtain their general scientific training in the Royal College of Science. The instruction in the Royal College of Science is arranged in such a manner as to give the Students a thorough training in the general principles of Science, followed by advanced instruction in one or more special branches of Science. The Associateship is granted in certain divisions or lines of study. Students who go through any one of the prescribed courses of instruction and pass the necessary Examinations receive a Certificate of Associateship of the Royal College of Science, or of the Royal School of Mines. Students who are not candidates for the Associateship are permitted to enter as occasional students in one or more special branches of science, and on passing the examination receive a Certificate to that effect. The Associateship of the Royal College of Science is given in one or more of the following divisions:—Mechanics, Physics, Chemistry, Biology, Geology, and Agriculture, and the Associateship of the Royal School of Mines in Metallurgy and Mining.

The course of instruction, which lasts for three years, is the same for all the divisions during the first year, after which it is specialised in accordance with the Scheme detailed in the Prospectus of the School.

The Session is divided into two Terms. The first Term begins on the 6th of October and ends about the middle of February. The second Term begins in the middle of February and ends about the middle of June.

Examinations are held at the end of each course of instruction and at such other periods as may be found necessary. On the results of these examinations the successful candidates are arranged in two classes, first and second. There are also "Honours" examinations for the subjects of the third year, the successful candidates being placed in order of merit. A student obtains the Associateship who passes in all the subjects of the first year, and, in the second and third year, those subjects prescribed as necessary for the division in which he seeks to obtain his Associateship. A student who goes through the prescribed course of instruction in any subject and passes the necessary examinations receives a certificate to that effect.

Students who do not wish to attend the lectures are admitted for short periods to the laboratories, at the discretion of the Professors. The fees for the laboratories are £4 per month.

Students not entering for the Associateship are admitted to any particular course of study, so far as there is room, on payment of the fees shown in the following table:—

	Lectures.	Laboratory.
	£	£
Chemistry	3	13
Physics	5	12
Biology with Botany	5	12
Geology with Mineralogy ..	4	8
Mechanics	4	6
Metallurgy	2	13
Mining	4	
Astronomical Physics	2	3

Agricultural Chemistry, per term, £13. Mathematics and Mechanical Drawing, £3 per term. Model and Freehand Drawing, £1 per term. Descriptive Geometry, £3 per session. Mine Surveying, £10.

The fees for the first two years amount to about £75, and for the remainder of the course for the Associateship they vary from £30 to about £40.

Both the private and the State-aided students are required to furnish themselves with certain instruments and apparatus before the commencement of the courses. These are enumerated in the syllabuses of the several subjects.

Officers of the Army, Navy, and Civil Service, recommended by their respective Departments, are admitted to the Lectures and Laboratories at half fees.

Associates of the Royal College of Science or of the Royal School of Mines have the privilege of free admission to the Library and to all the courses of lectures.

Bona fide teachers qualified to earn payments for teaching Science according to the rule of the Science and Art Directory may obtain permission to attend free any course of lectures.

Several valuable Exhibitions, Scholarships, and Prizes are attached to the studentship.

Summer Courses for Teachers.—Short courses of instruction are given annually, about July, in different branches of science for the benefit of teachers of science schools in the country. The courses last three weeks. About 250 teachers are admitted to them, and they receive third class railway fare to and from South Kensington, and a sum not exceeding £3 towards their expenses. (See Science and Art Directory).

Working Men's Lectures.—Notification of these will be given in the newspapers.

THE SCHOOL OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

The Fifty-seventh Session will commence on Monday, October 3rd, 1898.

Professors—Chemistry, J. Norman Collie, Ph.D., F.R.S. (Dean); Botany, J. Reynolds Green, Sc.D., F.R.S., F.L.S.; Materia Medica and Pharmacy, Henry G. Greenish, F.I.C., F.L.S.

A Course of Lectures on Physical, Inorganic, and Elementary Organic Chemistry commences in October and terminates at the end of June. An Advanced Course of Lectures begins in October and extends to the end of March. These Lectures are adapted to the requirements of Pharmaceutical and Medical Students, and also those who are proceeding to degrees at the University of London, or who are preparing for the examinations of the Institute of Chemistry.

Entries may be made for single classes. Certificates of attendance at the two Courses of Lectures on Chemistry and at the Chemical Laboratories are accepted as evidence of chemical training by the Institute of Chemistry in connection with the Examinations for the Associateship, and also by the conjoint Board of the Royal Colleges of Physicians and Surgeons, as well as by other examining bodies.

Prospectuses and further information may be obtained from Mr. Richard Bremridge, Secretary and Registrar, 17, Bloomsbury Square, London, W C.

UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.

University of Wales.

Professor—H. Ll. Snape, D.Sc. (Lond.), Ph.D. (Gœttingen), F.I.C.

Assistant Lecturer and Demonstrator—A. W. Warrington, M.Sc. (Vic.)., F.I.C.

Lecturer in Agricultural Chemistry—J. Alan Murray, B.Sc. (Edin.).

The College is open to male and female students above the age of sixteen years. The Session commences on Tuesday, October 4, on which day all Students will be expected to meet the Professors in the Examination Hall of the College.

Lecture Courses.—(1) Matriculation Course; three lectures weekly during the Michaelmas and two weekly during the Lent and Easter Terms. (2) Intermediate Science Pass Course; four lectures weekly during the Lent and Easter Terms. (3 and 4) B.Sc. Courses; A, three lectures weekly on Organic Chemistry; B, two lectures weekly on Chemical Theory. (Courses A and B will generally be given in alternate Sessions; for 1898-9, Course B.) (5 and 6) Courses in Agricultural Chemistry. For students in their first year, 3 lectures, and for those in their 2nd year, 2 lectures weekly throughout the Session.

Laboratory Courses.—The Laboratory is open daily from 10 a.m. to 1 p.m., and from 2.15 to 5 p.m., except on Wednesdays and Saturdays. Classes for the Systematic Study of Qualitative and Quantitative Analysis will be formed, and Special Courses will be arranged for those who intend to follow Medicine or Pharmacy, or any one particular branch of Applied Chemistry, always provided that such Students possess the requisite knowledge of Theoretical Chemistry. The hours will be arranged, as far as possible, to suit the requirements of the individual Student.

The College is recognised by the Royal University of Ireland, and by the Colleges of Physicians and Surgeons of England, Scotland, and Ireland as an institution at which the instruction necessary for their respective Diplomas in Medicine, in Chemistry, Physics, and Biology may be given. One year for graduation in Medicine and two years for graduation in Science may be spent at Aberystwyth.

Fees.—The Fee for the whole Session, if paid in advance, is £10; if paid by Single Terms, for the first term of attendance in each Session, £4; for the second term, £3 10s.; for the third term, £3. These composition fees enable the Student to attend any or all the Classes of the College, with the exception that a small extra fee is charged for Laboratory Instruction. Thus, for Practical Chemistry, the additional fee is, for six hours' work per week, 12s. 6d. per term, and for twelve hours, 25s. per term. The fees for those who desire to spend several days weekly in the laboratory may be learned on application to the Registrar. Fee for a single Lecture Course £1 per term.

Scholarships and Exhibitions varying in value from £10 to £40 per annum will be offered for competition at examinations which commence on September 20, and exhibitions are awarded at the end of the Session on the results of the class examinations.

The Chemical Laboratories in connection with this College have been recently built, and are fitted with every convenience for the prosecution of chemical studies.

Intending Students requiring further information are recommended to write to the Registrar for a copy either of the General Prospectus or of one of the Special Prospectuses issued for the Agricultural and Normal Departments.

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.

A Constituent College of the University of Wales.

Chemistry.—Professor, James J. Dobbie, M.A., D.Sc. Demonstrator, Fred. Marsden, Ph.D., M.Sc. Assistant Lecturer in Agricultural Chemistry, F. V. Dutton.

Physics. — Professor, Andrew Gray, M.A., LL.D., F.R.S.

The Session opens October 4th, 1898. All regular classes are open to men and women students above the age of 16 years. The following Courses of Lectures will be given.

Matriculation Course.—Subjects: Those prescribed for the Matriculation Examination of the University of Wales. Fee for the Session £3 3s.

Intermediate Course.—Inorganic Chemistry and Elementary Physical Chemistry. Fee for the Session, £3 13s. 6d.

B.Sc. Course.—Advanced Organic Chemistry. Fee for the Session, £3 3s.

Medical Course.—Fee, £4 4s.

Agricultural Chemistry.—Fee, £2 2s.

Laboratory Courses.—The laboratory is open on five days of the week from 10 a.m. to 4 p.m. for instruction in Chemical Analysis and in the Application of Chemistry to Medicine and the Industrial Arts. Fees: six hours per week, £1 1s. per Term; twelve hours, £2 2s.; eighteen hours, £3 3s.; twenty-four hours, £4 4s. Composition Fee for all Laboratory Classes of the Intermediate Science Course taken in one year, £4 4s.

The Chemistry, Botany, Zoology, and Physics Courses are recognised for Medical graduation in the Universities of Edinburgh and Glasgow, and students can make one *Annus medicus* at the college. The Science Courses are recognised for part of the science degree course of the University of Edinburgh.

UNIVERSITY COLLEGE OF SOUTH WALES AND MONMOUTHSHIRE, CARDIFF.

Professor—C. M. Thompson, M.A., D.Sc., F.C.S.

Demonstrators—E. P. Perman, D.Sc., F.C.S., and A. A. Read, F.I.C., F.C.S.

The Session commences October 3rd, and terminates on June 23rd, and is divided into three terms.

The Junior Course (delivered during the Michaelmas term only) consists of about 50 lectures, and will cover the subjects prescribed for the Matriculation examinations of the University of Wales and the University of London Fee, £2 2s. A revision class is held in the Summer term.

The Intermediate Course consists of about 80 lectures held during the Lent and Summer terms in continuation of the Junior Course, and is the qualifying course for the Intermediate Examination of the University of Wales. Together with laboratory practice, it will cover the subjects required for the Intermediate Examination in Science and the Prel. Sci. (M.B.) Examination of the University of London. Fee, £4 4s.

The Senior Course consists of some 90 lectures on Chemical Theory; Fee, £3 3s.

A course of 20 lectures on Qualitative Analysis and a short course on Organic Chemistry will also be given.

The following lectures on Metallurgy will be given by Mr. Read:—10 lectures on Fuel; Fee, 10s. 6d. 20 lectures on General Metallurgy; Fee, £1 1s. 30 lectures on the Manufacture of Iron and Steel; Fee, £1 1s. A practical course on Iron and Steel Analysis will also be held, and practical instruction in Dry Assaying will be given in the Metallurgical Laboratory, which is fitted with the necessary furnaces and apparatus.

In the laboratory each student works independently, so that the course of study may be adapted to the requirements of the individual. Hours, 9 to 1 and 2 to 5; Saturday, 9 to 1. Fees—Six hours per week, £3 3s. per session; twelve hours, £2 2s. per term; eighteen hours, £3 3s. per term; twenty-four hours £4 4s. per term.

Registered medical students can prepare for the Intermediate M.B. Examination of the University of London, and spend three out of their five years of medical study in Cardiff. Medical students wishing to graduate at a Scottish University, or preparing for a Conjoint Board Surgical and Medical Diploma, or for the Diploma of the Society of Apothecaries, can spend two years in Cardiff. For further information see the prospectus of the Faculty of Medicine, which may be obtained from the Registrar.

The College is recognised as an institution at which two years of the course for the degree of Bachelor of Science of the University of Edinburgh may be spent.

Students by making a payment of £10 at the commencement of each session may compound for all lecture fees for the whole session. Laboratory fees are not included in the composition fee, but Students preparing for the Science Examinations of the University of Wales and of the University of London may, by making a payment of £13 13s. at the commencement of each Session, compound for both Lecture and Laboratory Fees during the Session.

At the entrance examination in September, and the annual examination in June, several scholarships and exhibitions are awarded. Great importance is attached to special excellence in one subject.

The College Prospectus, and also further information as to scholarships, may be obtained from the Registrar.

A Hall of Residence for Women Students is attached to the College.

UNIVERSITY COLLEGE, BRISTOL.

Professor of Chemistry—Sydney Young, D.Sc., F.R.S.
Lecturer—Francis E. Francis, B.Sc., Ph.D.
Demonstrator—D. H. Jackson, M.A., B.Sc., Ph.D.

The session 1898-99 will begin on October 4th. Lectures and classes are held every day and evening throughout the Session. In the Chemical Department lectures and classes are given in all branches of theoretical chemistry, and instruction in practical chemistry is given daily in the chemical laboratory. The department of experimental physics includes various courses of lectures arranged progressively, and practical instruction is given in the physical and electrical laboratories. The Department of Engineering and the Constructive Professions is designed to afford a thorough scientific education to students intending to become engineers, or to enter any of the allied professions, and to supplement the ordinary professional training by systematic technical teaching. This department includes courses specially arranged for students intending to become civil, mechanical, electrical, or mining engineers, surveyors, or architects. Those who attend the mechanical engineering course enter engineering works during the six summer months, and, in accordance with this scheme, various manufacturing engineers in the neighbourhood have consented to receive students of the College into their offices and workshops as articled pupils at reduced terms. Medical education is provided by the Faculty of Medicine of the College. Several Scholarships are tenable at the College. Full information may be obtained from the Secretary.

DAY LECTURES.

Inorganic Chemistry.

The Courses treat of the principles of Chemistry, and of the Chemistry of the Non-Metals and Metals.

Junior Course.—Two Lectures a week will be given during the First and Second Terms. Fee, £3 3s.

General Elementary Science (London Matriculation).—A course of about 16 Lectures will be delivered in the Third Term. Fee, including Physics (1st and 2nd Terms), £5 5.

Special Course.—A special course of Lectures is also given to Engineering Students.

Senior Course.—Three Lectures a week will be given throughout the Session. Fee, £5 5s. There will be tutorial classes in connection with the Junior and Senior Courses.

Advanced Course (Parts I. and II.).—One Lecture a week will be given throughout the Session. Fee for each course, £2 12s. 6d.

Organic Chemistry.

This Course will relate to the more important groups of the Compounds of Carbon.

Two Lectures a week will be given during the Second Term, and three Lectures a week during the Third Term. Fee, £3 3s. An advanced course of lectures will also be given one day a week during the session. Fee, £2 12s. 6d.

Practical Chemistry.—Laboratory Instruction.

The Laboratory will be open daily from 10 a.m. to 5 p.m., except on Saturdays, when it will be closed. Instruction will be given in the Laboratory in all branches of Practical Chemistry, including Qualitative and Quantitative Inorganic and Organic Analysis, the preparation of Chemical Products, and Inorganic and Organic Research. Special facilities will be afforded to those who desire to study Practical Chemistry as applied to the different processes employed in the Arts and Manufactures. Fees in Guineas—

	5 Days a Week.	4 Days a Week.	3 Days a Week.	2 Days a Week.	1 Day a Week.
Per Session	15	12½	10	7½	5
,, Two Terms ..	11	9	7½	5½	3½
,, One Term ..	7	6	4½	3½	2½

Students may arrange to divide their days of laboratory work into half-days.

Chemical Scholarship.—Among others, a Chemical Scholarship of £25 is offered for competition.

EVENING LECTURES.

Two courses of Lectures will be delivered during the First and Second Terms; they will be devoted to the consideration of the general Principles of Chemistry and Chemical Physics and the Chemistry of Non-Metallic and Metallic Elements. Special attention will be paid throughout to those products which have a practical application in the Arts and Manufactures. Fee for each course, 7s. 6d.

General Elementary Science.—A course of Lectures, primarily intended for Candidates for Matriculation, will be given during the First Term. Fee (including Physics), 7s. 6d.

Practical Chemistry—Laboratory Instruction.—The Laboratory will be open on Tuesday and Wednesday evenings from 7 till 9. Instruction will be given in Qualitative and Quantitative Analysis, and in the Preparation of Chemical Products. Fees:—(Two Terms) Two Evenings, 25s.; One Evening, 15s. (One Term) Two Evenings, 15s.; One Evening, 10s 6d.

University College, Bristol, has been approved by the Council of the Institute of Chemistry as a College at which all the subjects required for the admission of Associates to the Institute are taught.

The Calendar of the College, price 1s. (post-free, 1s. 4d.), containing detailed information of the various Courses, may be obtained on application to the Secretary.

MASON COLLEGE, BIRMINGHAM.

Professor—Percy F. Frankland, Ph.D., B.Sc., F.R.S.
Assistant Lecturer—C. F. Baker, Ph.D., B.Sc.
Demonstrator—W. R. Innes, Ph.D., M.Sc.
Lecturer on Metallurgy—Godfrey Melland, F.I.C.

The Session will be opened on October 4th, 1898.

Elementary Course.

Forty Lectures adapted to the requirements of beginners will be given in the Winter and Spring Terms. Lecture days—Wednesdays and Fridays at 11.30.

Persons entirely unacquainted with Chemistry are recommended to attend this Course before entering for the General Course. Candidates for the Matriculation Examination of the University of London also are advised to attend this Course.

General Course.

The General Course of Lectures on Chemistry will be found useful by Students who are afterwards to become Engineers, Architects, Builders, Brewers, or Manufacturers (such as Metallurgists, Alkali, Soap, Manure, Glass, or Cement Makers, Bleachers and Dyers, &c.)

Students preparing for the Intermediate Examination in Science and Preliminary Scientific (M.B.) Examination of the University of London should attend the Lectures on Inorganic Chemistry (Winter and Spring Terms).

Candidates for Intermediate Examinations in Medicine will in general require only that part of the course (Summer Term) which relates to Organic Chemistry.

The full course, extending over three terms, will also satisfy the requirements of Students preparing for the Associateship of the Institute of Chemistry, so far as attendance at lectures on General and Theoretical Chemistry is concerned.

1. From October to March (Winter and Spring Terms). About eighty lectures on Inorganic Chemistry and Chemical Philosophy will be given on Mondays, Tuesdays, Wednesdays, and Thursdays from October to December, and on Mondays, Tuesdays, and Wednesdays from January to March, at 9.30 a.m. A Tutorial Class is held in connection with this Course once a week throughout the Session. Fee, £5 5s. for the course.

2. April to June (Summer Term). About thirty lectures will be given on Elementary Organic Chemistry, or the chemistry of the most important series of carbon compounds. This course will include all the subjects required for the Intermediate Examination in Medicine of the University of London. Lecture Days—Monday, Wednesday, and Friday at 12 noon Fee, £1 11s. 6d.

The General Course (including Inorganic and Organic lectures) qualifies for graduation in the medical faculties of the universities of Edinburgh, Glasgow, Aberdeen, and Durham.

Special Courses of Lectures and of Laboratory Instruction are given for Medical Students preparing for the Conjoint Board Examinations.

Advanced Course.

An Advanced Course for the study of Theoretical Chemistry and those parts of the subject which are required for the degree of B.Sc. in the University of London will meet twice a week. Fee for the session, £3 3s.

Laboratory Practice.

The College Laboratory is open daily from 9.30 to 5, except on Saturdays, when it is closed at 1 p.m.

Candidates for Intermediate Examination in Science, Preliminary Scientific (M.B.), B.Sc., and Intermediate Examination in Medicine of the University of London, may obtain in the Laboratory of the College the instruction necessary. The three months Course of Practical Chemistry for the B.Sc., Edinburgh, in the department of Public Health, may be taken in the Mason College Laboratory. Fees :—

	All day.	Three hours per day.
One Term	7 guineas	4½ guineas.
Two Terms	13 „	8½ „
Three Terms	18 „	12 „

A Course of short demonstrations and exercises is given by the Professor or one of his Assistants once a week. All first-year Students are required to attend, unless exempted for special reasons by the Professor. No Fee.

Metallurgy.

Three Courses of Ten Lectures will be given on the Principles and Practice of Metallurgy. Fee, 10s. 6d. for each of the first two courses, and for each of the two sections of the third course. A more advanced course of about sixty lectures upon selected subjects is also given.

There is a separate laboratory for metallurgical students in which provision is made for instruction in assaying, &c.

Evening Classes.

Special Courses of Evening Lectures are arranged during the Winter and Spring Terms of each session. The subjects are treated in a less technical manner and the fees are nominal.

Scholarships.

Priestley Scholarships.—Three Open Scholarships in Chemistry of the value of £100 each are awarded annually in September.

Bowen Scholarship.—One Open Scholarship in Metallurgy of the value of £100 is awarded annually in September.

Forster Research Scholarship.—A Scholarship of the value of £50 is annually awarded.

For particulars apply to the Registrar.

Excursions.

During previous Sessions permission has been obtained to visit some of the great factories in or near Birmingham, in which chemical and metallurgical industries are carried on. Students have thus had most valuable opportunities of gaining a practical acquaintance with some branches of Applied Science. The privilege thus courteously granted by several manufacturers will, it is hoped, be enjoyed in every future Session. The excursions will be conducted by the Professor or Lecturers.

BRADFORD TECHNICAL COLLEGE.

Chemistry and Dyeing Department.

Head Master—W. M. Gardner, F.C.S.
Demonstrator and Lecturer on Geology—A. B. Knaggs, F.C.S.
Lecturer on Botany and Biology—William West, F.L.S.

The College Session is divided into three terms. The Session commences on September 12th and terminates on July 15th. The course of instruction extends over three years, and embraces Lecture Courses on Inorganic and Organic Chemistry, the technology of the textile fibres, mordants, natural and artificial colouring matters, technical analysis, and laboratory practice in analytical chemistry, chemical preparations, and dyeing. Fee, £5 per Term, or £13 per Session.

During the first and second terms Evening Classes are held for the benefit of persons engaged during the day.

A General Course preparing for the Pharmaceutical Society's examinations has been arranged.

ROYAL AGRICULTURAL COLLEGE, CIRENCESTER.

Chemical Department.

Professor—Prof. E. Kinch, F.C.S., F.I.C.
Assistants—Cecil C. Duncan, F.I.C., and W. James.

Systematic courses of Lectures are given on the various branches of Chemistry in its relation to Agriculture, illustrated by experiments, and by the collections in the College

Museum. They comprise the laws of Chemical Combination and the general Chemistry of mineral bodies, and of the more frequently occurring bodies of organic origin, with the relationships of their leading groups; and, finally, the applications to practical operations of the Chemistry of the atmosphere, of soils and manures, of vegetation, of stock feeding, and of the processes and products of the dairy.

In the Laboratory practical instruction is given in the construction and use of apparatus and in Chemical manipulation and analysis, both qualitative and quantitative. After studying the simple operations and the properties of the commonly occurring substances, the Students are taught to analyse a series of compounds, and apply the knowledge thus obtained to the analysis of manures, soils, waters, feeding stuffs, dairy products, and other substances met with in the ordinary course of Agricultural practice. Chemico-agricultural researches are undertaken by the senior Students under the direction of the Professor and his Assistants.

VICTORIA UNIVERSITY.
THE YORKSHIRE COLLEGE, LEEDS.

Professor of Chemistry—Arthur Smithells, B.Sc. Lond., F.I.C.

Lecturer in Organic Chemistry—Julius B. Cohen, Ph.D., F.I.C.

Assistant Lecturer and Demonstrator—Herbert Ingle, F.I.C.

Demonstrators—T. S. Patterson, Ph.D., and J. McCrae, Ph.D.

The Session begins October 11, 1898.

Lecture Courses.

1. General Course of Chemistry.—Monday, Wednesday, and Friday, at 11.30 a.m. Fee for the Course, £4 4s.
2. Inorganic Chemistry.—First year Honours Course, Non-metals. Monday, Wednesday, and Friday, at 9.30 a.m. Fee, £3 13s. 6d.
3. Inorganic Chemistry. — Second year Honours Course, Metals. Tuesday, Thursday, and Saturday at 9.30 a.m. Fee, £3 13s. 6d.
4. Organic Chemistry. — Tuesday, Thursday, and Saturday at 12 noon Fee £3 13s. 6d.
5. Organic Chemistry Honours Course. — Wednesday and Friday at 12 noon. Fee, £2 12s. 6d.
6. Theoretical Chemistry.—Advanced Course. Tuesdays and Thursdays at 9.30 a.m. Fee, £2 12s. 6d.
7. Chemistry as Applied to Coal Mining.— Tuesday during the First Term, at 4 p.m.
8. Chemistry for Teachers.—Saturdays from 9.30 to 12.30 in the first and second terms. Fee, £4 4s.
9. Agricultural Chemistry.—Mondays, Wednesdays, and Fridays at 2 p.m.

Laboratory Courses.

The College Laboratory will be open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it will close at 1 p.m.

Fees for the Session—Students working six days per week, £21; five, £18 18s.; four, £16 16s.; three, £13 13s.

Class in Practical Chemistry, Saturday mornings, from 9.30 to 12.30. Fee £1 11s. 6d.

Practical Course in Sanitary Chemistry.—Tuesdays and Thursdays from 2 to 5 p.m., from January to March. Fee, £5 5s.

Evening Class.

A short Course of Lectures by Prof. Smithells, on the Chemistry of Artificial Lighting will be given during the first Term. Fee, 10s. 6d.

Dyeing Department.

Professor—J. J. Hummel, F.I.C.

Lecturer and Research Assistant — A. G. Perkin, F.R.S.E.

Assistant Lecturer—R. B. Brown.

This Course extends over a period of three years, and is intended for those who wish to obtain a full scientific and practical education in the art of dyeing. It is suitable for those who purpose in the future to take any part in the direction of the operations of dyeing or printing of textile fabrics, *e.g.*, the sons of manufacturers, calico printers, managers, master dyers, &c.

Leather Industries Department.

Professor—H. R. Procter, F.I.C.

Demonstrator—M. C. Lamb.

The full Course, which extends over a period of two years, is suitable to all who intend to become Technical Chemists in the Leather Industry, or managers of important works, and is recommended to sons of tanners. The Course includes instruction in chemistry, a modern language, leather manufacture, and practical work in the Leather Industries Laboratory and Dye-house.

Agricultural Department.

Professor—J. R. Campbell, B.Sc.

The full Course occupies two years, and includes instruction in chemistry, physics, mathematics, geology, botany, forestry, engineering and surveying, and the principles of agriculture, as well as practical work in the various laboratories and out door agriculture.

Research Students are admitted to the College Laboratories on reduced terms.

Several valuable Scholarships are at the disposal of the College, viz., the Salt, Akroyd, Brown, Emsley, Craven, Leeds City Council, and Clothworkers' Scholarships, and one of the 1851 Exhibition Scholarships. The West Riding County Council Scholarships are tenable at the Yorkshire College.

UNIVERSITY COLLEGE, LIVERPOOL.

Professor—J. Campbell Brown, D.Sc.

Lecturer on Organic Chemistry — C. A. Kohn, B.Sc., Ph.D.

Lecturer on Metallurgy—T. L. Bailey, Ph.D.

Demonstrators and Assistant Lecturers — T. L. Bailey, Ph.D., C. A. Kohn, B.Sc., Ph.D., and A. W. Titherley, M.Sc., Ph.D.

Assistant—H. H. Froysell.

The Session commences October 4th.

Entrance Scholarship Examination takes place early in May each year.

The William Gossage Chemical Laboratory has been completed and opened for Advanced Students, the Metallurgical Laboratory has been enlarged, and new Gas Analysis and Electro-Chemical rooms have been added, with a third Lecture Room.

The Classes meet the requirements of candidates for the Ordinary B.Sc. Degree, for Chemistry Honours, or for the M.Sc. or D.Sc. Degree in Victoria University; for Degrees in Medicine of Victoria, London, and Edinburgh; for the Pharmaceutical Diplomas; for a special Technological Certificate of University College; and for those studying Chemistry as a preparation for professional, technical, or commercial life. The Classes qualify for the Fellowship of the Institute of Chemistry of Great Britain and Ireland, and other Examination Boards.

Lecture Courses.

General Elementary Course on the principal non-metallic elements and the most important metals, the principles of Chemical Philosophy, and an introductory sketch of Organic Chemistry. Three Terms. Fee, £4.

Engineer's Course of Lectures with Practical Class. Two Terms. Fee, including Practical class, £4.

Pharmacy Courses: Junior, £3; Senior, £3.

Dental Course, Lectures and Practical. Fee, £5 5s.

Course A.—Non-metals. Fee, £3 10s.

Course B.—Metals. Fee, £3 10s.

Course C.—Organic Chemistry. Fee, £3 10s.

Course H.—Special Organic Subjects. Fee, £2.

Course D.—Physical Chemistry. Fee, £1.

Course E.—History of Chemistry and of the Development of Modern Chemical Philosophy. Three Terms. Fee, £2.

Courses F. — Applied Chemistry and Metallurgy: Lectures on Technology are given in connection with Laboratory work at hours to be arranged. The subjects are varied in different years. (1) Alkali and Allied Manufactures. (2) General Principles of Metullurgy. (3) Iron, Steel, and Aluminium. (4) Copper, Lead, Silver, and Gold, and other Metals. (5) Distillation of Coal and Tar Industries. (6) Fuel and Gas. (7) Chemistry Applied to Sanitation. (8) Technical Gas Analysis. (9) Electrochemical work. Three terms. Fee, each course £1 10s.

Practical Classes.

(1) Junior. (2) Intermediate: Qualitative Analysis of Inorganic Substances and of some of the more common Organic Substances. (3) Revision Class. (4) Senior: Practical Organic. (5) Practical Exercises on Technology, Pharmaceutical Chemistry, Saitanry subjects, Examination of Water and Air, of Animal Secretions, Urinary Deposits, Calculi, and Poisons. (6) Quantitative Class.

Chemical Laboratory.

The Chemical Laboratories provide accommodation for every kind of chemical and metallurgical work.

The William Gossage Laboratory, opened in 1897, consists of a large and well-fitted general Laboratory for advanced Students, a new gas analysis room, an additional lecture-room for Metallurgy and other classes, and an addition to the Research Laboratory. New stores for students' apparatus and chemicals have also been built and placed in charge of a skilled dealer.

Students desirous of gaining a thorough theoretical and practical acquaintance with Technical Chemistry, or who intend to adopt Chemical work as a profession, must devote three or four years to special study, for which a full curriculum is provided.

Table of Fees.

Per Week.	One Term, Three Months.	Three Terms, One Session.
One day	£4	£7
Two days	5 10s.	10
Three days	7	13
Four days	9	16 10s.
Whole week	10 10s.	21

Pharmaceutical Course (see special syllabus).

Technological Curriculum.

Preliminary Year.—Chemistry, the Elementary Course. Practical Classes 1 and 2. Mathematics, or Mechanics, Elementary Engineering, Drawing, and Design (in this or one of the following years). German. Or, the Victoria Preliminary Course and Examination may be taken.

First Year.—Chemistry—Courses A and B; Chemical Laboratory three days per week; Technological Chemistry, Course F. Physics, with laboratory work, one day per week. Mathematics (intermediate). German. Engineering, First Year Course, Autumn and Lent Terms. Intermediate B.Sc. Examination may be passed.

Second Year.—Chemistry, Lecture Course C, on Organic Chemistry, Lecture Course E or D, Technological Chemistry, Course F. Chemical Laboratory, four days per week. Engineering, Mathematics, or Physics (Advanced). The Final Examination for the Victoria B.Sc., or the Intermediate Examination of the Institute of Chemistry, may be taken.

Third Year.—Courses D, F, and H. Any other Courses omitted in a previous year. Laboratory, five days per week. Gas Analysis, Water Analysis, Electrochemistry. Students may finally choose a special subject either of research or of applied Chemistry. The Final Examination for the Associateship of the Institute of Chemistry of Great Britain and Ireland may be taken. Three years study after passing the Preliminary Examination of Victoria University are required for the B.Sc. Degree in the Honours School of Chemistry.

The Sheridan Muspratt Chemical Scholarship of £50 per annum, tenable for two years, will be competed for in December, 1898, on an Examination in subjects which are included in the first two and a half years of the above curriculum. Other Scholarships, Entrance Scholarships, and Free Studentships are also available to Students.

Evening Classes.

Classes, including laboratory work, will be held on Chemistry, Metallurgy, and on Electro-chemistry.

The Prospectus containing full particulars may be obtained from the Registrar, University College, Liverpool.

DURHAM COLLEGE OF SCIENCE, NEWCASTLE-ON-TYNE.

Professor of Chemistry—P. Phillips Bedson, M.A., D.Sc., F.I.C., F.C.S.

Lecturer in Chemistry—Saville Shaw, M.Sc., F.C.S.

Lecturer in Agricultural Chemistry—S. Hoare Collins, F.I.C., F.C.S.

Assistant Lecturer and Demonstrator—F. C. Garrett, M.Sc., F.C.S.

Demonstrator—J. Cooper, B.Sc.

The Session will commence on September 26th, 1898.

Lectures begin on October 4th, 1898.

1. *General Course.* — This Course of Lectures will extend over the three terms of the Session, and is intended to serve as an introduction to the Science. The Lectures will be of an elementary character, and whilst framed to meet the requirements of First Year Students will also be serviceable to such as intend pursuing Chemistry in its various applications in the arts and manufactures, as, for instance, Brewing, Metallurgy, the Manufacture of Soda, Soap, Glass, &c. The subjects treated will include an exposition of the Principles of Chemistry, and a description of the preparation and properties of the chief Elementary Substances, both metallic and non-metallic, and their more important native and artificial compounds. A section of this Course will be devoted to an outline of Organic Chemistry. The class will meet on Mondays, Wednesdays, and Fridays, at 11 a.m., and will commence on Wednesday, October 5th. Fee, £3 10s. for the Session.

Second Year Course.—The Lectures for the second year students cousist of a course of Lectures on Inorganic Chemistry, extending from October to December, and a course of Lectures on Organic Chemistry from January to the end of the Session. The Class will meet on Tuesdays and Thursdays at 11 a.m., and Fridays at 3 p.m., and will commence on October 6th. Fee for Session, £3 10s.; for Inorganic alone £1 10s.; and for Organic alone £3.

Advanced Classes will be formed for the study of Inorganic, Organic, and Theoretical Chemistry. Fee for the course, £3 10s.

A Lecture Course in Analytical Chemistry will be given on Mondays, at 3 p.m.

Metallurgy and Assaying.—Lecturer, Saville Shaw, M.Sc., F.C.S. A Metallurgical Laboratory is provided, in which instruction is given in the ordinary processes of Dry Assaying, and in the preparation and analysis of Alloys, &c. Fees as for Chemical Laboratory.

Agricultural Chemistry.—The instruction in this branch of Chemistry will consist of a series of Lectures and of special practical work in the Chemical Laboratory. Students will be expected to have a knowledge of Elementary Chemistry, such as may be obtained by attending the General Course.

The Lecture Course in Agricultural Chemistry is arranged for two days a week throughout the Session. Fee, £3 10.

Practical Chemistry.—The Laboratory is open from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it closes at 1 p.m. *Laboratory Fees.*—Students working two days, £2 10s. per term, £6 per session; one day per week, £1 10s. per term, £3 10s. per session.

Courses of Study.—Students will be divided into two classes:—(1) Regular, or Matriculated Students, who are also Members of the University of Durham; and (2) Non-Matriculated Students. Regular Students will be required to follow such a course of study in the subjects professed in the College as will enable them to pass the Examinations for the title of Associate in Physical Science of the University of Durham. Non-Matriculated Students will attend such classes as they may select. Every candidate for admission as a matriculated student must pass an examination on entrance, in reading, writing from dictation, English or Latin Grammar, arithmetic (including decimals), and geography. Registered students in medicine are exempted from this examination, or students who produce a certificate of having passed either of the two following examinations:—

1. Durham Examination for certificate of proficiency in General Education, held in March and September.

2. Durham Examination for Students in Arts in their first year, or any examination of a similar nature that may be accepted by the Council.

Associateship in Physical Science.—Every candidate for the Associateship in Physical Science will be required to satisfy the examiners in—Mathematics, Physics, Chemistry, and either Geology or Natural History—in an examination to be held at the end of the candidate's first year. Associates in Science are admissible one year after obtaining the title of Associate to examination for the degree of Bachelor of Science of the University of Durham.

Exhibitions.—Three Exhibitions of the value of £25, £15, and £10 respectively will be awarded in October next to Candidates desirous of attending the first year course of study in the College.

The examination will be held at the College, and will commence on Wednesday, September 29th.

Evening Lectures.—Courses of Evening Lectures will be given, with a Practical Class for Laboratory instruction.

Two Exhibitions of £15 each will be awarded at the next examination of "Persons not members of the University," which will be held at Durham in March next.

Several other valuable Scholarships are available for students, including Johnston Chemical Scholarship of the value of £60 for one year.

OWENS COLLEGE, VICTORIA UNIVERSITY, MANCHESTER.

Professor and Director of the Chemical Laboratory—Harold B. Dixon, M.A., F.R.S.

Professor of Organic Chemistry—W. H. Perkin, Ph.D., F.R.S.

Demonstrators and Assistant Lecturers—George H. Bailey, D.Sc., Ph.D.; W. A. Bone, D.Sc.; P. J. Hartog, B.Sc.; E. J. Russell, B.Sc.; and D. S. Jerdan, B Sc.

Demonstrator in Organic Chemistry—W. T. Lawrence, B.A., Ph.D.

Lecturer in Technical Organic Chemistry—Jocelyn F. Thorpe, Ph.D.

Assistant Lecturer in Metallurgy—J. Crowther.

The Session begins on October 4, 1898, and ends on July 1, 1899.

The instruction is given by means of Experimental Lectures and Tutorial Classes. The Chemical Classes form part of the Courses for Chemistry in the University.

Chemistry Lecture Courses.

General Chemistry Course.—Tuesdays, Thursdays, and Saturdays, at 9.30, during the two Winter Terms.

Introduction to Organic Chemistry.—Wednesdays and Fridays, at 9.30, during Lent Term.

These courses are intended for Medical Students and others beginning the study of chemistry.

First Year Honours Course.—Mondays, Wednesdays, and Fridays, 11.30 a.m., during the two Winter Terms. The Non-Metals.

Second Year Honours Course.—Mondays, Wednesdays, Fridays, 3.30 p.m., during the two Winter Terms. The Metals.

Third Year Honours Course.—At times to be arranged. Physical Chemistry.

Organic Chemistry (General).—Mondays and Fridays, 9.30, during two Winter Terms.

Organic Chemistry (Advanced).—Tuesdays and Thursdays, 9.30, during the two Winter Terms.

History of Chemistry and Chemical Philosophy.—Wednesdays, 9.30, during the Session.

Metallurgy.—*Lectures*: The Metallurgy of Copper, Lead, Silver, Gold, and the Metallurgy of Iron and Steel will be given in alternate years. *Practical*: The Laboratory will be open to students every day.

The Chemical Laboratories are open daily from 9.30. a.m. to 4.30 p.m., except on Saturdays, when they are closed at 12.30 p.m.

Courses for B.Sc. Degree.—To qualify for the B.Sc. Degree of the Victoria University, Students have to attend a prescribed course of study extending over three years, and to pass the Preliminary Examination of the University either on entering or at the end of a year's Course.

The Honours Course of Chemistry is as follows:—First year: First year Honours Lectures; Mathematics (3 hours a week); Physics (3 hours a week); a Language (3 hours a week); Chemical Laboratory (3 days per week). Second year: Second year Honours Lectures; General Organic Lectures; Applied Chemistry Lectures; Physics Laboratory (1 day per week); Chemical Laboratory (3 days per week). Third year: Third year Honours Lectures; Honours Organic Lectures; History of Chemistry Lectures; Chemical Laboratory (5 days per week).

The following awards are made to successful Students in the Honours Examination:—A University Scholarship of £50; a Mercer Scholarship of £25. A University Fellowship of £150 is awarded annually among the Graduates in Science for the encouragement of Research. Among the *College* Scholarships open to Chemical Students are the Dalton Chemical Scholarship, £50 per annum for two years; the 1851 Exhibition Scholarship; the John Buckley Scholarship; &c.

Applied Chemistry.

First Course.—Sulphuric Acid and Alkali Manufactures. General Principles of Chemical Engineering.

Second Course.—The Chemistry of Fuel. The Manufacture of Illuminating Gas and Gaseous Fuel.

Third Course.—Natural and Artificial Dye-stuffs, and the Principles of Dyeing and Printing.

Certificates in Applied Chemistry.

The course extends over a period of three years, and comprises systematic instruction by means of lectures and practical work in the laboratories.

Before admission to the first year's course students are required to give such evidence of elementary knowledge of Mathematics and Chemistry as shall be considered satisfactory by the Senate.

The first year's course is the same for all students working for the certificate.

In the second and third years a choice may be made between Inorganic and Organic Chemistry. By this division of the subject a student wishing to apply himself specially to the inorganic side of the science, may attend during his second year the Honours course in Metals, and courses on Geology or Mineralogy, and during his third year, courses on Metallurgy and on Geology or Mineralogy; while a student wishing to apply himself specially to the organic side of the science, may attend during his second and third years the Courses on Organic Chemistry, and courses on the Coal Tar Colours and on Dyeing and Printing.

Part of the Laboratory practice in the second and third years will consist in the examination and analysis of raw materials, products from chemical works, &c., in connection with the special courses of lectures on Applied Chemistry. In the Chemistry and Physical laboratories the practical work in the second year will be arranged in accordance with the branch of Chemistry selected by the candidate.

In the third year the student, if sufficiently advanced, will be set to work on some analytical process or problem in Applied Chemistry, under the direction of the teaching staff.

UNIVERSITY COLLEGE, NOTTINGHAM.

Departments of Chemistry and Metallurgy.

Professor of Chemistry—F. Stanley Kipping, Ph.D., D.Sc., F.I.C., F.R.S.

Demonstrators of Chemistry—J. J. Sudborough, D.Sc., Ph.D., F.I.C., and R. M. Caven, B.Sc., F.I.C.

The Classes of the College are open to students of both sexes above sixteen years of age.

The Session commences on October 10th.

Lecture Courses.—The Chemistry Day Lectures extend over three years. In the first year a student enters for the course on Elementary Inorganic Chemistry. In his second year he attends Lectures on both Inorganic and Organic Chemistry. In his third year he attends courses on Advanced Organic Chemistry, Physical Chemistry, and Advanced Inorganic Chemistry.

The fees for the Day Lectures and Classes are as follows: First year, two Lectures per week, 15s. per term. Second year, three Lectures per week, 22s. 6d. per term. Third year, four Lectures per week, 30s. per term.

Demonstrations and Lectures on Analytical Chemistry will be given in the day and evening, and should be attended by all students.

A Chemical Calculation Class is also held. Fee per Term, 5s.

Students may qualify themselves by attendance at these lectures and classes for the Examinations of the Universities of London, Cambridge, or Oxford, and for the Medical Examinations of the Royal College of Surgeons and of the Universities of Cambridge and Edinburgh: they may also obtain instruction in Chemistry for technical or other purposes, and can enter for a full Chemical Engineering Curriculum. Special attention is given to the requirements of candidates for the Associateship of the Institute of Chemistry.

Practical Chemistry and Metallurgy.—The Chemical and Metallurgical laboratories are open every day from 9 to 5, except on Saturday, when the hours are from 9 to 1; also on Tuesday and Thursday evenings from 7 to 9. Each Student works independently of other Students at a course recommended by the Professor. Instruction is given in general Chemical Manipulation, in Qualitative and Quantitative Analysis, and in the methods of Original Chemical Investigation and Research; Students are also enabled to work out the applications of Chemistry to Pharmacy, Metallurgy, Dyeing, Agriculture, Brewing, Iron and Steel, Tanning, and other Manufacturing Processes. Fees for day students: For one term, £7; for the session, £18; for six hours weekly 40s., and 5s. extra for each additional hour per week. For evening students, 10s. for two hours per week, three hours 15s., four hours 20s., six hours 30s., per term.

Research Work.—Students or others wishing to undertake research work in pure or Applied Chemistry will be afforded every facility for doing so and may be admitted at reduced fees. The Laboratories are fully equipped with apparatus and chemicals necessary for such work.

Courses of Technical Chemistry Lectures are also given on Engineering, Dyeing and Bleaching, Brewing, Plumbing, Bread-making, Gas Manufacture, and on other processes of applied Chemistry.

Pharmaceutical Students can at all times work in the Chemical Laboratory, taking work suitable for the preparation for the Minor Examinations. Special lectures will also be given in Chemistry and Materia Medica.

Government Lectures and Classes.—Evening Lectures and Laboratory instruction will be given by the Demonrators of Chemistry to Students who intend to present themselves for Examination by the Government Science and Art Department in May next. Inorganic, organic, and practical chemistry, agricultural chemistry, and metallurgy will be taught in the elementary, advanced, and honours stages, each of which commences at the beginning of the College Session in September. Fee for each Lecture Course, 5s.; for each Laboratory Course, 10s.

An Agricultural Course of instruction, extending over two years, is now organised under the general direction of Mr. M. J. R. Dunstan, M.A., F.R.S.E. It includes instruction in chemistry, botany, agriculture, with practical work on experimental fields, dairy work, farriery, land surveying, &c. The instruction is designed for those who intend to become farmers, bailiffs, land agents, or colonists, and may be extended to a third year if desired. Fee, £15 per annum for residents in Notts, £20 to residents in other counties.

Full information concerning all College Classes is given in the College Prospectus, price one penny.

UNIVERSITY COLLEGE, SHEFFIELD.

Professor of Chemistry—W. Carleton Williams, B.Sc., F.C.S.

Demonstrators and Lecturers— G. Young, Ph.D., and L. T. O'Shea, B.Sc., F.C.S.,

The Session will commence on October 6th.

Beginners' Course.— Inorganic Chemistry: Tuesday from 10 to 11 a.m. Fee, £1 11s. 6d.

Matriculation Course.—Friday 10 to 11. Fee, £1 11s. 6d.

Intermediate Course.—Inorganic Chemistry. Monday and Thursday from 10 to 11 a.m. £2 12s. 6d.

Organic Chemistry.—Elementary: Saturdays, 10 to 11; fee, £1 11s. 6d. Honours: Tuesdays and Thursdays, 12 to 1; fee, £2 12s. 6d. Advanced: Thursdays, 4 to 5; fee, £1 11s. 6d. Special Course: Hours to be arranged; £1 1s. Chemistry of the Colouring Matters: Fridays, 12 to 1; fee, £1 11s. 6d.

Physical Chemistry.—Monday, 11 to 12. Fee, £1 11s. 6d.

Chemical Philosophy. — Thursday, 11 to 12. Fee, £1 11s. 6d.

Short Courses of Lectures are also given by L. T. O'Shea on the Chemistry of Coal Mining.

A Course of Lectures is arranged for Medical Students, with a special class in Qualitative Analysis.

Laboratory.—Working hours to be arranged between Professor and Students.

Sessional Fees for Day Students:—Six hours per week, £5 5s.; Nine, £7; Twelve, £8 8s.; Eighteen, £11 5s.: Twenty-four, £14; Thirty-two, £17.

Day Students may not enter for less than six hours a week. Students joining the Laboratory at Christmas will be charged two-thirds and at Easter one-third of the Fees for the whole Session.

Fees for short periods (working thirty-two hours per week):—For one month, £3 3s.; two months, £5 5s.

An arrangement has been entered into with the Science and Art Department, South Kensington, which will enable Science Teachers to work in the Chemical Laboratory for three, six, or twelve hours a week on payment of one-quarter of the usual fee, the Department being willing to pay the remainder under certain conditions, of which full information may be obtained on application to the Registrar.

Evening Classes.—Lectures, Wednesday, 8 to 9. Laboratory instruction, Wednesday, 6 to 9, and another series to be arranged if desired. Sessional Fee, one evening per week, £1 10s.; two, 50s.; or Lecture Class and Laboratory, on Wednesday evening, £1 10s. Fee for one term, 17s. 6d.

UNIVERSITY COLLEGE, DUNDEE.

University of St. Andrews.

Professor of Chemistry—James Walker, Ph.D., D.Sc.

Assistant Lecturers—J. S. Lumsden, Ph.D., B.Sc., and J. K. Wood, B.Sc.

Lecture Assistant and Laboratory Steward—J. Foggie, F.C.S.

The Winter Session begins on October 12th, and ends on March 22nd. The Summer Session extends from the middle of April to the end of June.

The First Year's Lecture Course on Systematic Chemistry is given daily during the Winter Session, and embraces the Elements of Inorganic and of Organic Chemistry.

Advanced Courses, of about fifty lectures each, will be given during the year as follows:—

Organic Chemistry; Inorganic Chemistry, including the more important technological applications; Theoretical and Physical Chemistry; Bleaching and Dyeing, including the Chemistry of the Textile Fibres.

Practical Instruction in all of the above branches will be given in the Laboratories and Dye-house. Special facilities are afforded to Research Students.

The Lectures and Laboratory Practice in Chemistry are recognised by the Medical Colleges of London and Edinburgh. The Courses are suitable for the degrees of the University of London and for the Civil Service appointments, and will also satisfy the requirements of Students in Pharmacy, and of Students who intend to become candidates for the Associateship of the Institute of Chemistry, as far as qualification in Chemistry is concerned.

UNIVERSITY OF EDINBURGH.

Department of Chemistry.

Professor—Alex. Crum Brown, M.D., D.Sc., F.R.S.
Lecturers—L. Dobbin, Ph.D., and H. Marshall, D.Sc.
Assistants—W. W. Taylor, M.A., B.Sc., and J. P. Longstaff.

The working terms are—Winter Session, from middle of October to middle of March; Summer Session, from beginning of May to end of July.

Lecture Courses.—During the Winter Session a General Course of Chemistry for medical and science students is given by the Professor. The class meets daily; fee £4 4s. An Advanced Course of twenty-five lectures is also given in the Winter Session; fee, £2 2s. A class on Organic Chemistry is held in summer; fee, £2 2s. There is also a class on Chemical Theory, by Dr. Dobbin; fee £1 1s.: and a class on Mineralogy and Crystallography, by Dr. Marshall; fee, £2 2s. All these Lectures, except the General Course, are now open to women.

In addition to the above, Lecture Courses are given by the Assistants on some particular branch of Organic and Inorganic Chemistry. These Lectures are free to Laboratory Students.

Tutorial classes are held in connection with the General Course.

Laboratories.—Practical classes for Medical Students meet daily during the latter part of the Winter Session and in the Summer Session. (Fee, £3 3s.) The laboratories for analytical and advanced practical work are open daily from 9.30 till 4.30. (Fees: Whole Day—Winter Session, £10 10s., Oct.-Dec., Jan.-March; or Summer Session, £5 5s. Half Day—Winter Session, £6 6s., Oct.-Dec., Jan.-March; or Summer Session, £3 3s. Preference will be given to students in the above order. Students who are not Matriculated may attend the Chemical Laboratory on payment of the entrance fee of 5s. in addition to the Laboratory fees. Full Courses of instruction are given in Analytical, Practical Organic and Inorganic Chemistry, including Gas Analysis, Metallurgy, and Assaying. Facilities are afforded to advanced students who desire to undertake chemical investigations.

Various prizes and scholarships are attached to the laboratory and general class.

Graduation.—Two Degrees in Pure Science are conferred, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.).

Candidates for Degrees in Science, if not graduates (by examination) in Arts in one of the Universities of the United Kingdom or in a Colonial or Foreign University recognised for the purpose by the University Court, must pass a preliminary examination in (1) English; (2) Latin, Greek, French, or German; (3) Mathematics; (4) One of the languages Latin, Greek, French, German, Italian, not already taken under (2), or Dynamics. In the case of a student whose native language is other than European, the Senatus may, at the Preliminary Examination, accept such language as a substitute for a modern European language. The Senatus may also in such a case accept as an alternative to Latin or Greek any other classical languages, such as Sanscrit or Arabic.

The First B.Sc. Examination embraces Mathematics, or Biology (*i.e.*, Zoology and Botany), Natural Philosophy, and Chemistry. The Final B.Sc. Examination includes any three or more of the following subjects:—Mathematics, Natural Philosophy, Astronomy, Chemistry, Human Anatomy, including Anthropology, Physiology, Geology, including Mineralogy, Zoology, including Comparative Anatomy, and Botany, including Vegetable Physiology. In the Final Examination two written papers are set in each subject professed, the second of a higher standard than the first. Candidates must pass the first section in all, and the second section in at least one, of the subjects professed; the same regulations apply also to the Practical and Oral Examinations. Chemistry in this examination embraces Inorganic, including Mineralogical, Chemistry; Organic Chemistry; Chemical Crystallography; History of Chemistry. Practical Examination:—Complex Qualitative Analysis; Inorganic and Organic Preparations; Gravimetric and Volumetric Analysis. Each candidate taking the higher standard will also be examined on any two of the following subjects, selected by himself:—Ultimate Organic Analysis; Gas Analysis; Assaying; Physico-chemical Measurements.

A candidate for the D.Sc. Degree must submit a thesis on original work done by him. The Thesis must be approved before the candidate is allowed to proceed to Examination. The candidate in Chemistry may be required to pass a searching examination in one of the following branches:—(1) The Chemistry and Chemical Technology of Inorganic Bodies, including Metallurgy; (2) Organic Chemistry; and to show a thorough practical acquaintance with chemical analysis in all its branches, and with the preparation of pure substances.

HERIOT-WATT COLLEGE, EDINBURGH.

Principal—F. Grant Ogilvie, M.A., B.Sc.
Professor—John Gibson, Ph.D., F.R.S.E.
Demonstrators—Andrew F. King and James B. Shand.

The Session begins October 4th, 1898.

The curriculum of this College comprises both Day and Evening Classes, each department providing the higher general and technical education.

Chemistry.—The first course for day students is a combination of Lectures with Laboratory instruction. In the Lectures some of the more important elements and their compounds are discussed in detail, so as to lead to a knowledge of the general laws of chemical action. Other important elements are treated in less detail, and the relations and classification of the elements generally are broadly indicated. In the Laboratory each student will receive instruction in general chemical manipulation, in accurate weighing, volumetric measurements, and in some of the simpler methods of quantitative analysis. After making a series of simple preparations, he works through a number of experimental exercises illustrating chemical combination, oxidation, reduction, and double decomposition. These exercises are followed by instruction in simple methods of qualitative analysis, especial attention being given to dry way testing and the use of the spectroscope. Students attending a further course may take up the study of systematic analysis, and extend the knowledge they have gained of quantitative analysis by exercises in gravimetric, volumetric, and electrolytic methods. Ultimately they may make a speciality of any branch of the subject which may be most necessary for their future work. Great attention has been paid to the thorough equipment of Advanced Laboratories, and special facilities are given to advanced students who may wish to engage in any class of Research (Inorganic or Organic) whether of a purely chemical or of a technical nature.

The teaching in the Evening Classes is based on the

Syllabus of the Science and Art Department, and includes Elementary, Advanced, and Honours Courses in Theoretical and Practical Inorganic and Organic Chemistry.

GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

Professor of Chemistry—G. G. Henderson, D.Sc., M.A.
Professor of Technical Chemistry—E. J. Mills, D.Sc., F.R.S.
Agricultural Chemistry Lecturer—John W. Paterson, B.Sc., Ph.D.
Professor of Metallurgy—A. Humboldt Sexton, F.C.S., F.R.S.E.

Also, Professors and Lecturers in the other leading branches of Pure and Applied Science and Technology.

The main objects of this College are to afford a suitable education to those who wish to qualify themselves for following an industrial profession or trade, and to train teachers for technical schools. It was founded by an Order in Council, dated 26th November, 1886, according to a scheme framed by the Commissioners appointed under the provisions of the Educational Endowments (Scotland) Act, whereby Anderson's College, the Young Chair of Technical Chemistry in connection with Anderson's College, the College of Science and Arts, Allan's Glen's Institution, and the Atkinson Institution were placed under the management of one governing body.

The Diploma of the College is awarded to Day Students who have attended prescribed courses of instruction and passed the necessary examinations. The ordinary courses extend over three years, but arrangements are made for advanced students continuing their studies in special departments.

Complete courses of instruction in Metallurgy and Mining will be given in both Day and Evening Classes.

Copies of the Calendar for 1896-97 may be had from Mr. John Young, B.Sc., the Secretary, 38, Bath Street, Glasgow, price by post, 1s. 4d.

UNIVERSITY OF ST. ANDREWS.

United College of St. Leonard and St. Salvator.

Professor of Chemistry — T. Purdie, B.Sc., Ph.D., LL.D., F.R.S.

The Session begins on October 12th. A Competitive Examination, open to intending Students of Arts, Science, and Medicine, for about fifty Entrance Bursaries, ranging in value from £40 to £10 each per annum, will be held on September 30th and following days. About thirty of these Bursaries are restricted to Men and about twenty to Women, the latter being intended for women who at the conclusion of their Arts or Science Course will proceed to Medicine. Two, of £40 each are open to students of either sex. Two Scholarships of £100 each, tenable for one year, will be open for competition to Graduates of Science at the close of Session 1897-98. A Hall of Residence is provided for Women Students. Two Degrees in Science are conferred by the University of St. Andrews, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.), and Chemistry is also included in the curriculum for the M.A. Degree; the regulations will be found in the "University Calendar."

Lecture Courses.

Two distinct Courses of Lectures are given, each comprising at least one hundred meetings of the class.

First Year's Course.—This Class meets at 11 o'clock on five days in the week. The introductory lectures treat of the Nature of Chemical Action, the Classification of Substances into Elements and Compounds, the Phenomena of Oxidation, and the Composition of Air and Water. The Laws of Chemical Combination and the Atomic Theory are next discussed, after which the more commonly occurring elements and inorganic compounds are described systematically. Elementary Organic Chemistry is also included in the Course.

The chemistry of manufactures is referred to only cursorily; special attention, on the other hand, is given to those parts of the science which are of general educational value, and as much of the theory of chemistry is introduced as is compatible with elementary treatment. The Lectures are supplemented by a short Course of Laboratory Practice, intended to illustrate the principles of the science.

These courses of instruction are intended to meet the requirements of the Arts' Curriculum; also of candidates for the First B.Sc. Examination, and of students of medicine, so far as Theoretical Chemistry is concerned.

Second Year's Course.—The first part of the Course is devoted to Organic Chemistry, and the second part treats of the General Principles and Theory of Chemistry, and of more advanced Inorganic Chemistry, the instruction in general being such as is required for the Second B.Sc. Examination.

Certificates are awarded on the results of examinations, and the "Forrester Prize" of about £10 is awarded to the best Student of the year.

Fee for the Session, for each Course, £3 3s.

Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., except on Saturdays, when it is closed at 1 p.m. The work pursued in the Laboratory comprises:—(1) The performance of experiments illustrative of the Principles of Inorganic and Organic Chemistry; (2) Qualitative and Quantitative Analysis; (3) Original Investigation. Each student pursues an independent course of study under the supervision of the Professor or Demonstrator, the nature of the work varying with the proficiency of the student and the particular object he may have in view. Suitable courses of instruction in Practical Chemistry are provided for candidates for the First and Second B.Sc. Examinations, and for Students of Medicine.

The fees for Practical Chemistry vary according to the number of hours taken weekly. A certain number of working places in the Laboratory will be available without fee for students who are capable of undertaking original investigation.

QUEEN'S COLLEGE, BELFAST.

Professor—E. A. Letts, Ph.D., D.Sc., F.R.S.E., &c.

The Session commences on Tuesday, October 19, 1897.

I.—*Chemistry.*—The lectures are delivered at 3 p.m., on the first five days of each week, and terminate at the end of March The course is divided into three parts:—(1) Chemical Philosophy; (2) Inorganic Chemistry; (3) Organic Chemistry. Fee, £2.

II.—*Practical Chemistry.*—In this course the Students are instructed in the general methods of conducting Chemical Analyses. Fee, £3.

III.—*Laboratory Pupils.*—The Chemical Laboratory is open from November until the end of March, and from May 1st until the third week of July, on the first five days of the week, from 10 a.m. until 4 p.m. Students are admitted as working pupils on payment of a fee of £5 for the first period, or of £3 10s. for the second period (or for a single term).

Scholarships.—In addition to various Scholarships awarded in the Faculties of Arts and Medicine in which Chemistry forms a part of the examination, there are other valuable Scholarships awarded specially in connection with the schools of Chemistry and Physics.

QUEEN'S COLLEGE, CORK.

Professor—Augustus Edward Dixon, M.D.
Demonstrator—R. E. Doran, F.C.S.

The College Session begins on October 18th, 1898, and ends on June 10th, 1899. The classes are open to male and female students.

Systematic Chemistry.—(1) General course of Inorganic Chemistry, Elementary Organic Chemistry, and Chemical

Philosophy.—Fee for each Sessional Course, £2. Each subsequent Course, £1. (2) Advanced Organic Chemistry, and Chemical Philosophy.

Practical Chemistry.—(1) Two ordinary Courses of Practical Chemistry will be held, each of three months' duration; one commencing on January 5th, 1899, and adapted to the requirements of Students proceeding to the Examinations of the Royal University of Ireland; the other ending about the third week in June, and suitable for Medical Students intending to present themselves for the Examinations of other Licensing Bodies. Fee for each Sessional Course, £3. (2) A Course for Pharmaceutical Students will be held in the second and third terms; fee, £5. (3) Special Courses.

The Chemical Laboratory is open daily from 10 to 4 o'clock (except during class hours and on Saturdays) under the Superintendence of the Professor, to Students entering for special courses of qualitative and quantitative analysis; organic chemistry; or for the purpose of original investigation.

QUEEN'S COLLEGE, GALWAY.

Professor—Alfred Senier, Ph.D., M.D., F.I.C.
Demonstrator—W. S. Mills.

The College Session, 1898-99, commences October 18th and ends June 10th.

Chemistry is studied by attendance at Lectures, by work in the Laboratories, and by the use of the College Library. The Courses in the several faculties are arranged with a view to the requirements of the Royal University of Ireland, but are adapted also to those of other Universities and licensing bodies.

Lecture Courses. Faculty of Arts. — 1. Second year's Course, Inorganic and the Elements of General Chemistry. 2. Third year's Course, Advanced Organic Chemistry. 3. Fourth year's Post-Graduate Course, Advanced General Inorganic and Organic Chemistry. *Faculty of Medicine.* — First year's Course, Inorganic and Elementary Organic Chemistry. *School of Engineering.*—First year's Course, Inorganic Chemistry.

Laboratory Courses. Faculty of Arts. — 1. Second year's Course, Exercises in Inorganic Qualitative Analysis. 2. Third year's Course, Quantitative Analysis and other experiments to suit the requirements of individual Students. 3. Fourth year's Post-Graduate Course, Advanced Quantitative Analysis, Organic and Inorganic Preparations, and determination of their Physical and Chemical characters. 4. The Laboratories are also open to Students for work in other branches of Chemistry. *Faculty of Medicine.* — 1. Second year's Course, Inorganic and Organic Elementary Qualitative Analysis, and the Chemical Examination of Urine. *School of Engineering.* —1. Second year's Course, Inorganic Qualitative Analysis.

For Fees, Regulations as to Scholarships, and other particulars apply to the Registrar, from whom the Calendar, published in December, and the Extracts from Calendar, published in advance in July, may be obtained.

ROYAL COLLEGE OF SCIENCE FOR IRELAND,
STEPHEN'S GREEN, DUBLIN.
(SCIENCE AND ART DEPARTMENT).

Professor of Chemistry—W. N. Hartley, F.R.S.
Assistant Chemist—Hugh Ramage, F.I.C., Associate of the Royal College of Science, Dublin.
Demonstrator of Chemistry and Assaying — J. Holms Pollok, B.Sc.

The Session commences on Tuesday, October 6th, 1898.

The Royal College of Science for Ireland supplies, as far as practicable, a complete course of instruction in Science applicable to the Industrial Arts, and is intended also to aid in the instruction of teachers for the local Schools of Science.

Diplomas are awarded in the Faculties of Mining, Engineering, and Manufactures, Physics, and Natural Science. If accompanied by a certificate from the Professor of Chemistry, the Diploma of Associate of the Royal College of Science in the Faculty of Manufactures is recognised by the Council of the Institute of Chemistry of Great Britain and Ireland as qualifying candidates for admission to the practical examinations of the Institute.

The instruction in Chemical Science includes (1) General Chemistry; (2) Advanced Chemistry, including Chemical Manufactures and Metallurgy; (3) Analytical and Experimental Chemistry; (4) Instruction in Chemical Research.

Fees payable by Non-Associates:—£2 for each separate Course of Lectures. For Analytical Chemistry and Research—£2 for a special course of one month; £5 for three months; £9 for six months; £12 for the entire session. For Assaying—£5 for three months; £9 for six months £12 for the entire session.

The following are supplementary courses of instruction arranged for those who are attending a Course of Lectures:—

(1) Laboratory Instruction in the Theory of Chemistry. (2) An Analytical Course for Students in Engineering. (3) A Course of Practical Chemistry for Medical Students. (4) The Analysis of Water, Air, Food, and Drugs, intended for the instruction of Public Analysts and Medical Officers of Health. (5) Assaying. (6) A Course of Chemistry for Pharmaceutical Students.

There are four Royal Scholarships of the value of £50 each yearly, with Free Education, including Laboratory Instruction, tenable for two years; two become vacant each year; they are awarded on the results of their examinations to Associate Students, not being Royal Exhibitioners, who have been a year in the College. There are also nine Royal Exhibitions attached to the College, of the yearly value of £50 each, with Free Education, including Laboratory Instruction, tenable for three years; three become vacant each year, and are competed for at the May Examinations of the Department of Science and Art.

CHEMICAL LECTURES, CLASSES, AND LABORATORY INSTRUCTION.

City and Guilds of London Institute for the Advancement of Technical Education.—The operations of the City and Guilds of London Institute are divided broadly into four branches: the educational work of three London Colleges, and of the Technological Examinations. Programmes of the London Colleges may be had on application to the Head Office of the Institute, Gresham College, Basinghall Street, London, E.C., or from the respective Colleges. The Technological Examinations (Examinations Department, Exhibition Road, S.W.), are conducted once every year at various centres throughout the kingdom. Programme, with Syllabus of Subjects, &c., may be obtained of Messrs. Whittaker and Co., Paternoster Square, London, or through any bookseller, price 10d., net. — *City and Guilds Technical College, Exhibition Road.*—Professor of Chemistry, H. E. Armstrong, Ph.D., F.R.S. The object of this Institution is to give to London a College for the higher technical education, in which advanced instruction shall be provided in those kinds of knowledge which bear upon the different branches of productive industry, whether Manufactures or Arts. The main purpose of the instruction given is to practically demonstrate the application of different branches of science to various manufacturing industries. In order that this instruction may be efficiently carried out, the Institution, in addition to the lecture theatres and class rooms, is fitted with laboratories, drawing offices, and workshops; and opportunities are afforded for the prosecution of original research, with the object of the more thorough training of the students, and for the elucidation of the theory of industrial processes. The courses of instruction are arranged to suit the requirements of—1. Persons who are training to become

Technical Teachers; 2. Persons who are preparing to enter Engineers' or Architects' offices, or Manufacturing works; 3. Persons who desire to acquaint themselves with the scientific principles underlying the particular branch of industry in which they are engaged. The Matriculation Examinations will begin on Tuesday, Sept. 20th, and the Winter Session opens on Monday, October 3rd. *City and Guilds Technical College, Finsbury.*—Professor of Chemistry, Raphael Meldola, F.R.S. The operations of the Technical College, Finsbury, are divided into two distinct portions: Day Classes for those who are able to devote one, two, or three years to systematic technical education; Evening Classes for those who are engaged in industrial or commercial occupations in the daytime and who desire to receive supplementary instruction in the application of Science and of Art to the trades and manufactures in which they are concerned or employed. Each Professor is assisted by Demonstrators. Besides these there are Lecturers and Teachers in special subjects. An examination for the admission of Students will be held at the College at 10 o'clock on Tuesday, September 20th, 1898. *South London Technical Art School.*—Classes in Modelling, Design, Drawing and Painting from the Life, and House Decoration.

City of London College, White Street, Moorfields.—Courses of Evening Lectures and Laboratory Practice in Chemistry and Physics, conducted by Mr. I. S. Scarf, F.I.C., F.C.S., assisted by Messrs. H. W. Harrie, F.C.S., and C. A. West, A.R.C.S., F.C.S. Session commences September 28.

Battersea Polytechnic.—Principal, Mr. Sidney H. Wells, Wh. Sc. Inorganic, Organic, and Technological Chemistry, Mr. John Wilson, M.Sc. (Vict.), assisted by Mr. John L. White, M.Sc., and Mr. B. C. Polkinghorne, B.Sc. Day and Evening Classes in Science and Art subjects.

Birkbeck Literary and Scientific Institution, Bream's Buildings, Chancery Lane. — Chemistry Courses will be conducted, commencing September 26, adapted for the Elementary, Advanced, and Honours Examinations of the Science and Art Department, and for the Matriculation, B.Sc., and M.B. Degrees of the London University, by Mr. J. E. Mackenzie, Ph.D., B.Sc.

Borough Polytechnic Institute, St. George's Circus.—Lecturer, Mr. F. Mollwo Perkin, Ph.D. Lectures and Laboratory work in Chemistry and Physics. Session commences Monday, September 26, 1898.

Brixton School of Chemistry and Pharmacy, 12, Knowle Road, Brixton.—Dr. A. B. Griffiths, F.R.S.E., F.C.S., &c. The Lectures and Classes are adapted to the requirements of Pharmaceutical and Medical Students, and also those who are proceeding to Degrees at the University of London. Medals and certificates are awarded to successful students. The Laboratory is fitted with every convenience for the prosecution of chemical studies and research. Prospectuses and further information may be obtained from the Principal.

South-West London Polytechnic, Manresa Road, Chelsea.—Principal, Herbert Tomlinson, B.A., F.R.S. Technical Day Classes in Chemical Industries, commencing September 26th.

The Goldsmiths' Institute, New Cross, S.E.—Head of the Chemistry Department, Mr. W. J. Pope; Assistants, Mr. S. J. Peachy and others. Lectures and Practical Classes in General Chemistry, also in Chemistry applied to Gas Manufacture and other industries, are held in the evenings from 7.30 to 10.0, and are open to both sexes. Special attention is paid to Technical Laboratory work and the investigation of manufacturing difficulties.

Polytechnic Institute, 309, Regent Street, London, W.—Mr. R. A. Ward and Assistants.—Evening Classes in Theoretical and Practical Chemistry, &c.. The Classes are open to both sexes. The next term commences on Monday, September 26th.

Northern Polytechnic Institute, Holloway, N.—Principal, J. T. Dunn, D.Sc. Session begins September 30th. Evening Classes in Theoretical and Practical Chemistry. Assistants, Mr. H. Charles L. Bloxam and Mr. W. H. Watson, A.R.C.S.

Carpenters' Company Technical Institute, Jupp Road, Stratford, E.—Principal, William Ping. F.C.S. Session begins Monday September 26th. Evening Classes in Theoretical and Practical Chemistry, and in many other Departments of Science and Art. Day Technical School.

East London Technical College, People's Palace, E.—Chemistry: Professor, J. T. Hewitt, M.A., D.Sc., Ph.D.; Demonstrator, F. G. Pope; Assistants, H. A. Phillips and A. J. Turner. Lectures and Practical Classes are held in the daytime in connection with the three years' course of the Day Technical College. Evening Classes are also held, offering instruction in the courses of the Science and Art Department and for the examinations of the University of London.

University Tutorial College, 32, Red Lion Square, Holborn, W.C. (Science Department of the Univ. Corr. Coll.).—Chemical, Biological, and Physical laboratories, open both during term and vacation. Morning, Afternoon, and Evening Classes. Students may work either for long or short periods, either for examination or for private practice. The Laboratories accommodate over 100 Students.

South London School of Pharmacy, Lim., 325, Kennington Road, S.E.—Lectures on Chemistry and Physics, by Dr. John Muter, F.R.S.E., F.I.C., and Mr. J. Thomas, B.Sc. (Lond.), Daily, at 12 noon. Lectures on Botany daily at 1 p.m. and at 2.30 p.m. on Materia Medica and Pharmacy, by Mr. Dodd, F.C.S. The Students' Laboratory of this Institution is specially designed to accommodate 40 Students. The Technical Laboratory is open daily from 9 till 5, and is fully fitted with all apparatus for teaching the manufacture of drugs and chemicals. Periodical Examinations of the Students are held by Visiting Examiners appointed by the Council of Education, and Medals and Certificates are awarded on the results thereof. Fees for the first three months 12 guineas; afterwards 3 guineas per month, inclusive of all departments.

Imperial College of Chemistry and Pharmacy, 51, Imperial Buildings, Ludgate Circus.—Mr. F. Davis, B.Sc.

Metropolitan College of Pharmacy, 162, Kennington Park Road, S.E.—Principal, W. Watson Will, F.C.S.

Westminster College of Chemistry and Pharmacy. Trinity Square, Borough, S.E. — Messrs. Wills and Wootton. Day and Evening Classes.

The Clifton Laboratory, Berkeley Square, Bristol.—Principal, E. H. Cook, D.Sc. (Lond.), F.I.C. Students are received either as Private Pupils or Members of a Class. Instruction is given to those requiring to use science or scientific methods in Commercial and Industrial pursuits, or in preparing for Examinations. Students are urged to undertake researches and receive special attention from the teachers. Every effort is made to produce thorough chemists rather than successful examinees.

Leeds Technical School (of the Institute of Science, Art, and Literature), Cookridge Street, Leeds.—Head Master, R. E. Barnett, B.Sc.(Lond.), A.R.C.S. Evening Classes are held in 30 subjects of Science and Technology, among which are:—Chemistry, Inorganic and Organic, Theoretical and Practical, by Mr. R. E. Barnett, B.Sc., A.R.C.S., and Mr. R. W. Ferguson, A.R.C.S.; Metallurgy, Theoretical and Practical, by Mr. B. A. Burrell, F.I.C., F.C.S.; Magnetism and Electricity, Heat, and Practical Physics, by Mr. J. E. Tindall, B.Sc. Fees:—Lectures, from 2s. 6d. per Session; Laboratory work, from 7s. 6d. Session commences September 12. Prospectuses of various Classes and the complete Syllabus of the School free on application to the Secretary, Leeds Institute.

The Municipal Technical School, Princess Street, Manchester.—At this important Municipal School, with an attendance of upwards of 3500 Students, there are organised Day Courses in Pure Chemistry, with applications to Dyeing, Bleaching, Printing, Brewing, and Metallurgy. In addition there are Evening Courses, not only in Pure Chemistry, but in Metallurgy, Mineralogy, Iron and Steel Manufacture, Brewing, Bleaching , Dyeing, and Printing, Coal Tar Products, Paper Manufacture, Gas Analysis, Gas Manufacture, Chemical Engineering, Chemistry for Engineers and Builders, and Photography. The complete Syllabus (4d., by post 6d.) may be obtained on application to Mr. J. H. Reynolds, Director and Secretary, Princess Street, Manchester.

The Manchester Colege of Pharmacy, Oxford Street, Manchester.—Director, Mr. Charles Turner, F.C.S. Classes and Lectures specially designed to meet the requirements of Pharmaceutical Students.

Chemical and Bacteriological Laboratory, Barton Arcade, Manchester. — Mr. George J. Allen, F.C.S.— Special Instruction and Practice in Applied Science.

Higher Grade School, Patricroft.—Science and Art Day and Evening School, and Institute for Women. Demonstrator in Chemistry, Mr. R. J. B. Sanderson.

The School of Mines, Redruth, Cornwall.—Principal and Instructor in Inorganic Chemistry, Assaying, and Mineralogy, Mr. I. Paul de Castro, B.H. (Cantab). Instructor in Mining, Thomas Collins. Instructor in Panning and Vanning, Captain W. Hambly. Instructor in Mine Surveying, Captain F. Wickett.

Sheffield Pharmaceutical and Chemical Society·—Botany and Chemistry (Theoretical and Practical), are conducted by the Professors of, and at, Firth's College, West Street, Sheffield, commencing first week in October. The Materia Medica and Pharmacy at the Society's Rooms, 37, New Surrey Street, commencing first week in October.

Hartley College, Southampton. — Principal, R. Wallace Stewart, D.Sc. (Lond.). London University Courses in Arts and Science, Science Courses for Medical and Dental Students, Mechanical and Electrical Engineering Courses. Session commences Tuesday, September 27, 1898.

Stockport Technical School. — Department of Chemistry and Dyeing.—Principal: Mr. R. J. Brown, M.Sc. A syllabus with full particulars of the courses of instruction, hours, fees, &c., is obtainable on application. Special instruction is given in the Dyeing of Felt, &c., as applied to Hat Manufacture.

Technical Institute, Salford.—Principal, W. Wilson, M.A. Session begins September 13th. Special attention is directed to the Dyeing and Calico Printing Laboratories. Day and Evening Classes.

Aberdeen University.—Prof. Japp.

School of Medicine, Edinburgh.—Dr. S. Macadam, Mr. King, Mr. I. Macadam, and Drs. Aitken and Readman.

St. Mungo's College and School of Medicine, Edinburgh.—Dr. Marshall.

Surgeon's Hall, Nicolson Street, Edinburgh.—Dr. Stevenson Macadam, Lecturer. Classes for Medical and General Students. Lectures commence Tuesday, October 12, 1897.

Glasgow University.—Prof. J. Ferguson.

Anderson's College, Glasgow.—Mr. J. R. Watson.

Veterinary College, Buccleuch Street, Glasgow.—Prof. T. S. Goodwin.—Session, October to May. Systematic Lectures on Inorganic and Organic Chemistry, daily, 12 to 1; Laboratory, daily, 10 to 5. Special Laboratory Courses arranged for Agricultural Students, October to April.

Royal College of Surgeons in Ireland, Dublin.—Professor of Chemistry and Hygiene: Sir Charles A. Cameron, M.D., F.R.C.S.I. Instruction is given in the College Laboratory in General, Practical, and Analytical Chemistry, and in the subjects (Physical, Chemical, and Microscopical) required for Examinations in Public Health and to educate for the position of Public Analyst.

OBITUARY.

Dr. JOHN HOPKINSON, F.R.S.

The terrible accident by which Dr. Hopkinson and three of his children have just lost their lives in Switzerland, has occurred with such appalling suddenness that it is hard to realise that never again will he be seen in scientific circles.

By his death we lose not only an eminent electrician, mathematician, and engineer, but also a personal friend, whose energy, keen perception, and sound reasoning make the news of his untimely death the more startling.

Dr. Hopkinson was born in the year 1849, and received the first part of his education at Owens College, Manchester; in 1870 he took his degree as Doctor of Science at the London University. In the following year he took the Smith Prize, and attained the position of Senior Wrangler at Cambridge.

His work in electrical engineering is vast and well known; he has originated and carried out many schemes of electric traction and lighting, which will not allow his name to be forgotten.

He was the author of many works on scientific subjects, a member of the Board of Managers of the Royal Institution, a member of the Council of the British Association, twice President of the Institution of Electrical Engineers, besides belonging to other scientific societies.

THE CHEMICAL NEWS.

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BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

Bristol, 1898.

INAUGURAL ADDRESS OF THE PRESIDENT,

Sir William Crookes, F.R.S., V.P.C.S.

For the third time in its history the British Association meets in your City of Bristol. The first meeting was held under the presidency of the Marquis of Lansdowne in 1836, the second under the presidency of Sir John Hawkshaw in 1875. Formerly the President unrolled to the meeting a panorama of the year's progress in physical and biological sciences. To-day the President usually restricts himself to specialities connected with his own work or deals with questions which for the time are uppermost. To be President of the British Association is unundoubtedly a great honour. It is also a great opportunity and a great responsibility; for I know that, on the wings of the Press, my words, be they worthy or not, will be carried to all points of the compass. I propose first to deal with the important question of the supply of bread to the inhabitants of these Islands, then to touch on subjects to which my life work has been more or less devoted. I shall not attempt any general survey of the sciences; these so far as the progress in them demands attention will be more fitly brought before you in the different sections either in the Addresses of the Presidents or in communications from Members.

Before proceeding with my address I wish to refer to the severe loss the British Association has sustained in the death of Lord Playfair. With Sir John Lubbock and Lord Rayleigh, Lord Playfair was one of the Permanent Trustees of our Association, and for many years he was present at our meetings. It would be difficult to overrate his loss to British science. Lord Playfair's well-matured and accurate judgment, his scientific knowledge, and his happy gift of clothing weighty thoughts in persuasive language, made his presence acceptable, whether in the council chamber, in departmental enquiries, or at light social gatherings, where, by the singular laws of modern society, momentous announcements are sometimes first given to the world. Lord Playfair (then Sir Lyon Playfair) was President of the British Association at Aberdeen in 1885; his Address on that occasion will long be remembered as a model of profound learning and luminous exposition.

And now I owe a sort of apology to this brilliant audience. I must ask you to bear with me for ten minutes, for I am afraid what I now have to say will prove somewhat dull. I ought to propitiate you, for to tell the truth, I am bound to bore you with figures. Statistics are rarely attractive to a listening audience; but they are necessary evils, and those of this evening are unusually doleful. Nevertheless when we have proceeded a little way on our journey I hope you will see that the river of figures is not hopelessly dreary. The stream leads into an almost unexplored region, and to the right and left we see channels opening out, all worthy of exploration, and promising a rich reward to the statistic explorer who will trace them to their source,—a harvest, as Huxley expresses it, "immediately convertible into those things which the most sordidly practical of men will admit to have value, namely, money and life." My chief subject is of interest to the whole world—to every race—to every human being. It is of urgent importance to-day, and it is a life and death question for generations to come. I mean the question of Food supply. Many of my statements you may think are of the alarmist order; certainly they are depressing, but they are founded on stubborn facts. They show that England and all civilised nations stand in deadly peril of not having enough to eat. As mouths multiply, food resources dwindle. Land is a limited quantity, and the land that will grow wheat is absolutely dependent on difficult and capricious natural phenomena. I am constrained to show that our wheat-producing soil is totally unequal to the strain put upon it. After wearying you with a survey of the universal dearth to be expected, I hope to point a way out of the colossal dilemma. It is the chemist who must come to the rescue of the threatened communities. It is through the laboratory that starvation may ultimately be turned into plenty.

The food supply of the kingdom is of peculiar interest to this meeting, considering that the grain trade has always been, and still is, an important feature in the imports of Bristol. The imports of grain to this city amount to about 25 million bushels per annum—eight millions of which consist of wheat.

What are our home requirements in the way of wheat? The consumption of wheat per head of the population (unit consumption) is over 6 bushels per annum; and taking the population at 40 millions, we require no less than 240 million bushels of wheat, increasing annually by two million bushels to supply the increase of population. Of the total amount of wheat consumed in the United Kingdom we grow 25 and import 75 per cent.

So important is the question of wheat supply that it has attracted the attention of Parliament, and the question of national granaries has been mooted. It is certain that, in case of war with any of the great Powers, wheat would be contraband, as if it were cannon or powder, liable to capture, even under a neutral flag. We must therefore accept the situation and treat wheat as munitions of war and grow, accumulate, or store it as such. It has been shown that at the best, our stock of wheat and flour amounts only to 64,000,000 bushels—fourteen weeks' supply—while last April our stock was equal to only 10,000,000 bushels, the smallest ever recorded by "Beerbohm" for the period of the season. Similarly, the stocks held in Europe, the United States, and Canada, called "the world's visible supply," amounted to only 54,000,000 bushels, or ten millions less than last year's sum total, and nearly 82 millions less than that of 1893 or 1894 at the corresponding period. To arrest this impending danger, it has been proposed that an amount of 64,000,000 bushels of wheat should be purchased by the State and stored in national granaries, not to be opened, except to remedy deterioration of grain, or in view of national disaster rendering starvation imminent. This 64 million bushels would add another fourteen weeks' life to the population; assuming that the ordinary stock had not been drawn on, the wheat in the country would only then be enough to feed the population for twenty-eight weeks.

I do not venture to speak authoritatively on national granaries. The subject has been discussed in the daily press, and the recently published Report from the Agricultural Committee on National Wheat Stores brings together all the arguments in favour of this important scheme, together with the difficulties to be faced if it be carried out with necessary completeness.

More hopeful, although difficult and costly, would be the alternative of growing most, if not all of our own wheat supply here at home in the British Isles. The average yield over the United Kingdom last year was 29·07 bushels per acre; the average for the last eleven years being 29·46. For twelve months we need 240,000,000 bushels of wheat, requiring about 8½ million acres of good wheat-growing land, or nearly 13,000 square miles, increasing at the rate of 100 square miles per annum, to render us self-supporting as to bread food. This area is about one-fourth the size of England.*

A total area of land in the United Kingdom equal to a plot 110 miles square, of quality and climate sufficient to grow wheat to the extent of 29 bushels per acre, does not seem a hopeless demand.† It is doubtful, however, if this amount of land could be kept under wheat, and the necessary expense of high farming faced, except under the imperious pressure of impending starvation, or the stimulus of a national subsidy or permanent high prices. Certainly these 13,000 square miles would not be available under ordinary economic conditions, for much, perhaps all the land now under barley and oats would not be suitable for wheat. In any case, owing to our cold, damp climate and capricious weather, the wheat crop is hazardous, and for the present, our annual deficit of 180,000,000 bushels must be imported. A permanently higher price for wheat is, I fear, a calamity that ere long must be faced. At enhanced prices, land now under wheat will be better farmed, and therefore will yield better, thus giving increased production without increased area.

The burning question of to-day is what can the United Kingdom do to be reasonably safe from starvation in presence of two successive failures of the world's wheat harvest, or against a hostile combination of European nations. We eagerly spend millions to protect our coasts and commerce; and millions more on ships, explosives, guns, and men; but we omit to take necessary precautions to supply ourselves with the very first and supremely important munition of war—food.

To take up the question of food-supply in its scientific aspect, I must not confine myself exclusively to our own national requirements. The problem is not restricted to the British Isles—the Bread-eaters of the whole world share the perilous prospect—and I do not think it out of place if on this occasion I ask you to take with me a wide general survey of the wheat supply of the whole world.

Wheat is the most sustaining food grain of the great Caucasian race, which includes the peoples of Europe, the United States, British America, the white inhabitants of South Africa, Australasia, parts of South America, and the white population of the European Colonies. Of late years the individual consumption of wheat has almost universally increased. In Scandinavia it has risen 100 per cent in twenty-five years; in Austro-Hungary, 80 per cent; in France, 20 per cent; while in Belgium it has increased 50 per cent. Only in Russia and Italy, and possibly Turkey, has the consumption of wheat per head declined.

In 1871 the bread-eaters of the world numbered 371,000,000. In 1881 the numbers rose to 416,000,000, in 1891 to 472,600,000, and at the present time they number 516,500,000. The augmentation of the world's bread-eating population in a geometrical ratio is evidenced by the fact that the yearly aggregates grow progressively larger. In the early seventies they rose 4,300,000 per annum, while in the eighties they increased by more than 6,000,000 per annum, necessitating annual additions to the bread supply nearly one-half greater than sufficed twenty-five years ago.

How much wheat will be required to supply all these hungry mouths with bread? At the present moment it is not possible to get accurate estimates of this year's wheat crops of the world, but an adequate idea may be gained from the realised crops of some countries and the promise of others. To supply 516,500,000 bread-eaters, if each bread-eating unit is to have his usual ration, will require a total of 2,324,000,000 bushels for seed and food. What are our prospects of obtaining this amount?

According to the best authorities the total supplies from the 1897 98 harvest are 1,921,000,000 bushels.* The requirement of the 516,500,000 bread-eaters for seed and food are 2,324,000,000 bushels; there is thus a deficit of 403,000,000 bushels, which has not been urgently apparent owing to a surplus of 300,000,000 bushels carried over from the last harvest. Respecting the prospects of the harvest year just beginning it must be borne in mind that there are no remainders to bring over from last harvest; we start with a deficit of 103,000,000 bushels and have 6,500,000 more mouths to feed. It follows, therefore, that one-sixth of the required bread will be lacking unless larger drafts than now seem possible can be made upon early produce from the next harvest.†

The majority of the wheat crops between 1882 and 1896 were in excess of current needs, and thus considerable reserves of wheat were available for supplementing small deficits from the four deficient harvests. But bread-eaters have almost eaten up the reserves of wheat, and the 1897 harvest being under average, the conditions become serious.‡ That scarcity and high prices have not prevailed in recent years is due to the fact that since 1889 we have had seven world crops of wheat and six of rye abundantly in excess of the average. These generous crops increased accumulations to such an extent as to obscure the fact that the harvests of 1895 and 1896 were each much below current requirements. Practically speaking, reserves are now exhausted, and bread-eaters must be fed from current harvests—accumulation under present conditions being almost impossible. This is obvious from the fact that a harvest equal to that of 1894 (the greatest crop on record, both in acre-yield and in the aggregate) would yield less than current needs.§

It is clear we are confronted with a colossal problem that must tax the wits of the wisest. When the bread-eaters have exhausted all possible supplies from the 1897-98 harvest, there will be a deficit of 103,000,000 bushels of wheat, with no substitution possible unless Europeans can be induced to eat Indian corn or rye bread. Up to recent years the growth of wheat has kept pace with demands. As wheat-eaters increased, the acreage under wheat expanded. The world has become so familiarised with the orderly sequence of demand and supply, so accustomed to look upon the vast plains of other wheat-growing countries as inexhaustible granaries, that in a light-hearted way it is taken for granted that so many million additional acres can be added year after year to the wheat-growing area of the world. We forget that the wheat-growing area is of strictly limited extent, and that a few million acres regularly absorbed soon mount to a formidable number.

The present position being so gloomy, let us consider future prospects. What are the capabilities as regards available area, economic conditions, and acreage yield of the wheat-growing countries from whence we now draw our supply?

For the last thirty years the United States have been the dominant factor in the foreign supply of wheat, exporting no less than 145,000,000 bushels. This shows how the bread-eating world has depended, and still depends, on the United States for the means of subsistence. The entire world's contributions to the food-bearing area have averaged but 4,000,000 acres yearly since 1869. It is scarcely possible that such an average, under existing conditions, can be doubled for the coming twenty-five years.‖ Almost yearly, since 1885, additions to the wheat-growing area have diminished, while the requirements of the increasing population of the States have advanced, so that the needed American supplies have been drawn from the acreage hitherto used for exportation. Practically there remains no uncultivated prairie land in the United States suitable for wheat-growing. The virgin

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* Appendix A.

† The total area of the United Kingdom is 120,979 square miles; therefore the required land is about a tenth part of the total.

* Appendix B.

† Appendix C.

‡ Appendix D.

§ Appendix E.

‖ Appendix F.

land has been rapidly absorbed, until at present there is no land left for wheat without reducing the area for maize, hay, and other necessary crops.*

It is almost certain that within a generation the ever increasing population of the United States will consume all the wheat grown within its borders, and will be driven to import, and, like ourselves, will scramble for a lion's share of the wheat crop of the world. This being the outlook, exports of wheat from the United States are only of present interest and will gradually diminish to a vanishing point. The enquiry may be restricted to such countries as probably will continue to feed bread-eaters who annually derive a considerable part of their wheat from extraneous sources.

But if the United States, which grow about one-fifth of the world's wheat and contribute one-third of all wheat exportations, are even now dropping out of the race, and likely soon to enter the list of wheat-importing countries, what prospect is there that other wheat-growing countries will be able to fill the gap, and, by enlarging their acreage under wheat, replace the supply which the States have so long contributed to the world's food? The withdrawal of 145 million bushels will cause a serious gap in the food supply of wheat-importing countries, and unless this deficit can be met by increased supplies from other countries, there will be a dearth for the rest of the world after the British Isles are sufficiently supplied.

Next to the United States, Russia is the greatest wheat exporter, supplying nearly 95 million bushels.†

Although Russia at present exports so lavishly, this excess is merely provisional and precarious. The Russian peasant population increases more rapidly than any other in Europe. The yield per acre over European Russia is meagre—not more than 8·6 bushels to the acre—while some authorities consider it as low as 4·6 bushels. The cost of production is low—lower even than on the virgin soils of the United States. The development of the fertile though somewhat over-rated "black earth" which extends across the southern portion of the empire and beyond the Ural Mountains into Siberia progresses rapidly. But, as we have indicated, the consumption of bread in Russia has been reduced to danger point. The peasants starve and fall victims to "hunger typhus," whilst the wheat-growers export grain that ought to be consumed at home.

Considering Siberia as a wheat grower, climate is the first consideration. Summers are short—as they are in all regions with Continental climates north of the 45th parallel,—and the ripening of wheat requires a temperature averaging at least 65° F. for fifty-five to sixty-five days. As all Siberia lies north of the summer isotherm of 65°, it follows that such region is ill adapted to wheat culture unless some compensating climatic condition exists. As a fact, the conditions are exceptionally unfavourable in all but very limited districts in the two westernmost governments. The cultivable lands of Western Siberia adapted to grain bearing neither equal in extent nor in potential productive powers those of Iowa, Minnesota, and Nebraska. There are limited tracts of fair productiveness in Central Siberia and in the valleys of the southern affluents of the Amoor, but these are only just capable of supporting a meagre population.

Prince Hilkoff, Russian Minister of Ways and Communications, declared in 1896 that "Siberia never had produced, and never would produce, wheat and rye enough to feed the Siberian population." And, a year later, Prince Krapotkin backed the statement as substantially correct.

Those who attended the meeting of the British Association last year in Canada must have been struck with the extent and marvellous capacity of the fertile plains of Manitoba and the North-West Provinces. Here were to be seen 1,290,000 acres of fine wheat-growing land, yielding 18,261,950 bushels, one-fifth of which comes to hungry England. Expectations have been cherished that the Canadian North-West would easily supply the world with wheat, and exaggerated estimates are drawn as to the amount of surplus land on which wheat can be grown.* Thus far, performance has lagged behind promise, the wheat-bearing area of all Canada having increased less than 500,000 acres since 1884, while the exports have not increased in greater proportion. As the wheat area of Manitoba and the North-West has increased, the wheat area of Ontario and the Eastern provinces has decreased; the added acres being little more than sufficient to meet the growing requirements of population. We have seen calculations showing that Canada contains 500,000,000 acres of profitable wheat land. The impossibility of such an estimate ever being fulfilled will be apparent when it is remembered that the whole area employed in both temperate zones for growing all the staple food crops is not more than 580,000,000 acres, and that in no country has more than 9 per cent of the area been devoted to wheat culture.†

The fertility of the North-West Provinces of the Dominion is due to an exceptional and curious circumstance. In winter the ground freezes to a considerable depth. Wheat is sown in the spring, generally April, when the frozen ground has been thawed to a depth of three inches. Under the hot sun of the short summer the grain sprouts with surprising rapidity, partly because the roots are supplied with water from the thawing depths. The summer is too short to thaw the ground thoroughly, and gate-posts or other dead wood extracted in autumn are found still frozen at their lower ends.

Australasia as a potential contributor to the world's supply of wheat affords another fertile field for speculation. Climatic conditions limit the Australian wheat area to a small portion of the southern littoral belt. Professor Shelton considers there are still fifty million acres in Queensland suitable for wheat, but hitherto it has never had more than 150,000 acres under cultivation. Crops in former days were liable to rust, but since the Rust in Wheat conferences and the dissemination of instruction to farmers, rust no longer has any terrors. I am informed by the Queensland Department of Agriculture that of late years they practically have bred wheat vigorous enough to resist this plague. For the second season in succession the wheat crop last year was destroyed over large areas in Victoria; and in South Australia the harvest averaged not more than about 3¾ bushels per acre, after meeting Colonial requirements for food and seed, leaving only 684,000 bushels for export. In most other districts the yield fails to such an extent as to cause Europeans to wonder why the pursuit of wheat raising is continued.

New Zealand has a moist climate resembling that of central and southern England, while South Australia is semi-arid, resembling western Kansas. Only two countries in the world yield as much wheat per acre as New Zealand—these are Denmark and the United Kingdom. Notwithstanding the great yield of wheat due to an equable climate, New Zealand finds fruit and dairy farming still more profitable. The climatic conditions favourable to wheat are also conducive to luxuriant growths of nutritious grasses. Thus the New Zealander ships his butter more than half-way round the world and competes successfully with western Europe.

During the last twenty-seven years the Austro-Hungarian population has increased 21·8 per cent as against an increase of 54·6 per cent in the acreage of wheat. Notwithstanding this disparity in the rates of increase, exports have practically ceased by reason of an advance of nearly 80 per cent in unit consumption. There can be little doubt that Austro-Hungary is about to enter the ranks of importing nations, although in Hungary a con-

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* Appendix G.

† Appendix H.

* Appendix I.

† Appendix J.

siderable area of wheat land remains to be brought under cultivation.*

Rumania is an important wheat-growing country. In 1896 it produced 69,000,000 bushels, and exported 34,000,000 bushels. It has a considerable amount of surplus land which can be used for wheat, although for many years the wheat area is not likely to exceed home requirements.

As a producer of wheat France comes next to the United States, but for our purpose she counts but little, being dependent on supplies from abroad for an average quantity of 14 per cent of her own production. There is practically no spare land in France that can be put under wheat in sufficient quantity to enable her to do more than provide for increase of population.

Germany is a gigantic importer of wheat, her imports rising 700 per cent in the last twenty-five years, and now averaging 35,000,000 bushels. Other nations of Europe also importers do not require detailed mention, as under no conceivable conditions would they be able to do more than supply wheat for the increasing requirements of their local population, and, instead of replenishing, would probably diminish, the world's stores.

The prospective supply of wheat from Argentina and Uruguay has been greatly over-rated. The agricultural area includes less than 100,000,000 acres of good, bad, and indifferent lands, much of which is best adapted for pastoral purposes. There is no prospect of Argentina ever being able to devote more than 30,000,000 acres to wheat; the present wheat area is about 6,000,000 acres, an area that may be doubled in the next twelve years. But the whole arable region is subject to great climatic vicissitudes, and to frosts that ravage the fields south of the 37th parallel. Years of systematised energy are frustrated in a few days —perhaps hours—by a single cruelty of Nature, such as a plague of locusts, a tropical rain, or a devastating hail storm. It will take years to bring the surplus lands of Argentina into cultivation, and the population is even now insufficient to supply labour at seed time and harvest.

During the next twelve years, Uruguay may add a million acres to the world's wheat fields; but social, political, and economic conditions seriously interfere with agricultural development.

At the present time South Africa is an importer of wheat, and the regions suitable to cereals do not exceed a few million acres. Great expectations have been formed as to the fertility of Mashonaland, the Shire Highlands, and the Kikuyu plateau, and as to the adaptation of these regions to the growth of wheat. But wheat culture fails where the banana ripens, and the banana flourishes throughout central Africa, except in limited areas of great elevation. In many parts of Africa insect pests render it impossible to store grain, and without grain stores there can be little hope of large exports.

North Africa, formerly the granary of Rome, now exports less than 5,000,000 bushels of wheat annually, and these exports are on the decline owing to increased home demands. With scientific irrigation, Egypt could supply three times her present amount of wheat, although no increase is likely unless the cotton fields of the Delta are diverted to grain growing. In Algeria and Tunis nearly all reclaimed lands are devoted to the production of wine, for which a brisk demand exists. Were this land devoted to the growth of wheat an additional five million bushels might be obtained.

The enormous acreage devoted to wheat in India has been declining for some years, and in 1895 over 20,000,000 acres yielded 185,000,000 bushels. Seven-eighths of this harvest is required for native consumption, and only one-eighth on an average is available for export. The annual increase of population is more than 3,000,000, demanding an addition to the food-bearing lands of not less than 1,800,000 acres annually. In recent years the increase has been less than one-fourth of this amount.†

In surveying the limitations and vicissitudes of wheat crops I have endeavoured to keep free from exaggeration and have avoided insistance on doubtful points. I have done my best to get trustworthy facts and figures, but from the nature of the case it is impossible to attain complete accuracy. Great caution is required in sifting the numerous varying current statements respecting the estimated areas and total produce of wheat throughout the world. The more closely official estimates are examined the more defective are they found, and comparatively few figures are sufficiently well established to bear the deductions often drawn. In doubtful cases I have applied to the highest authorities in each country, and in the case of conflicting accounts have taken data the least favourable to sensational or panic-engendering statements. In a few instances of accurate statistics their value is impaired by age; but for 95 per cent of my figures I quote good authorities, while for the remaining 5 per cent I rely on the best commercial estimates derived from the appearance of the growing crops, the acreage under cultivation, and the yield last year. The maximum probable error would make no appreciable difference in my argument.

The facts and figures I have set before you are easily interpreted. Since 1871, unit consumption of wheat, including seed, has slowly increased in the United Kingdom to the present amount of 6 bushels per head per annum; while the rate of consumption for seed and food by the whole world of bread-eaters was 4·15 bushels per unit per annum for the eight years ending 1878 and at the present time is 4·5 bushels. Under present conditions of low acre yield, wheat cannot long retain its dominant position among the food-stuffs of the civilised world. The details of the impending catastrophe no one can predict, but its general direction is obvious enough. Should all the wheat-growing countries add to their area to the utmost capacity, on the most careful calculation the yield would give us only an addition of some 100,000,000 acres, supplying at the average world-yield of 12·7 bushels to the acre, 1,270,000,000 bushels, just enough to supply the increase of population among bread-eaters till the year 1931.*

At the present time there exists a deficit in the wheat area of 31,000 square miles,—a deficit masked by the fact that the ten world crops of wheat harvested in the ten years ending 1896 were more than 5 per cent above the average of the previous twenty-six years.

When provision shall have been made, if possible, to feed 230,000,000 units likely to be added to the bread-eating populations by 1931,— by the complete occupancy of the arable areas of the temperate zone now partially occupied—where can be grown the additional 330,000,000 bushels of wheat required ten years later by a hungry world? What is to happen if the present rate of population be maintained, and if arable areas of sufficient extent cannot be adapted and made contributory to the subsistence of so great a host?

Are we to go hungry and to know the trial of scarcity? That is the poignant question. Thirty years is but a day in the life of a nation. Those present who may attend the meeting of the British Association thirty years hence will judge how far my forecasts are justified.

If bread fails not only us but all the bread-eaters of the world—what are we to do? We are born wheat-eaters. Other races, vastly superior to us in numbers, but differing widely in material and intellectual progress, are eaters of Indian corn, rice, millet, and other grains; but none of these grains have the food value, the concentrated health sustaining power of wheat, and it is on this account that the accumulated experience of civilised mankind has set wheat apart as the fit and proper food for the development of muscle and brains.

It is said that when other wheat-exporting countries realise that the states can no longer keep pace with the demand, these countries will extend their area of cultiva-

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* Appendix K.

† Appendix L.

* Appendix M,

tion, and struggle to keep up the supply *pari passu* with the falling off in other quarters. But will this comfortable and cherished doctrine bear the test of examination?

Cheap production of wheat depends on a variety of causes, varying greatly in different countries. Taking the cost of producing a given quantity of wheat in the United Kingdom at 100*s*., the cost for the same amount in the United States is 67*s*., in India 66*s*., and in Russia 54*s*. We require cheap labour, fertile soil, easy transportation to market, low taxation and rent, and no export or import duties. Labour will rise in price, and fertility diminish as the requisite manurial constituents in the virgin soil become exhausted. Facility of transportation to market will be aided by railways, but these are slow, and costly to construct, and it will not pay to carry wheat by rail beyond a certain distance. These considerations show that the price of wheat tends to increase. On the other hand, the artificial impediments of taxation and customs duties tend to diminish as demand increases and prices rise.

I have said that starvation may be averted through the laboratory. Before we are in the grip of actual dearth the Chemist will step in and postpone the day of famine to so distant a period that we, and our sons and grandsons, may legitimately live without undue solicitude for the future.

It is now recognised that all crops require what is called a "dominant" manure. Some need nitrogen, some potash, others phosphates. Wheat pre-eminently demands nitrogen, fixed in the form of ammonia or nitric acid. All other necessary constituents exist in the soil; but nitrogen is mainly of atmospheric origin, and is rendered "fixed" by a slow and precarious process which requires a combination of rare meteorological and geographical conditions to enable it to advance at a sufficiently rapid rate to become of commercial importance.

There are several sources of available nitrogen. The distillation of coal in the process of gas-making yields a certain amount of its nitrogen in the form of ammonia; and this product, as sulphate of ammonia, is a substance of considerable commercial value to gas companies. But the quantity produced is comparatively small; all Europe does not yield more than 400,000 annual tons, and, in view of the unlimited nitrogen required to substantially increase the world's wheat crop, this slight amount of coal ammonia is not of much significance. For a long time guano has been one of the most important sources of nitrogenous manures, but guano deposits are so near exhaustion that they may be dismissed from consideration.

Much has been said of late years, and many hopes raised by the discovery of Hellriegel and Wilfarth that leguminous plants bear on their roots nodosities abounding in bacteria endowed with the property of fixing atmospheric nitrogen; and it is proposed that the necessary amount of nitrogen demanded by grain crops should be supplied to the soil by cropping it with clover and ploughing in the plant when its nitrogen assimilisation is complete. But it is questionable whether such a mode of procedure will lead to the lucrative stimulation of crops. It must be admitted that practice has long been ahead of science, and for ages farmers have valued and cultivated leguminous crops. The four-course rotation is turnips, barley, clover, wheat,—a sequence popular more than two thousand years ago. On the Continent, in certain localities, there has been some extension of microbe cultivation; at home we have not reached even the experimental stage. Our present knowledge leads to the conclusion that the much more frequent growth of clover on the same land, even with successful microbe-seeding and proper mineral supplies, would be attended with uncertainty and difficulties. The land soon becomes what is called "clover sick" and turns barren.

There is still another and invaluable source of fixed nitrogen. I mean the treasure locked up in the sewage and drainage of our towns. Individually the amount so lost is trifling, but multiply the loss by the number of inhabitants, and we have the startling fact that, in the United Kingdom, we are content to hurry down our drains and water courses into the sea, fixed nitrogen to the value of no less than £16,000,000 per annum. This unspeakable waste continues, and no effective and universal method is yet contrived of converting sewage into corn. Of this barbaric waste of manurial constituents Liebig, nearly half a century ago, wrote in these prophetic words: —"Nothing will more certainly consummate the ruin of England than a scarcity of fertilisers—it means a scarcity of food. It is impossible that such a sinful violation of the divine laws of Nature should for ever remain unpunished; and the time will probably come for England sooner than for any other country, when, with all her wealth in gold, iron, and coal, she will be unable to buy one-thousandth part of the food which she has, during hundreds of years, thrown recklessly away."

The more widely this wasteful system is extended, recklessly returning to the sea what we have taken from the land, the more surely and quickly will the finite stocks of nitrogen locked up in the soils of the world become exhausted. Let us remember that the plant creates nothing; there is nothing in bread which is not absorbed from the soil, and unless the abstracted nitrogen is returned to the soil, its fertility must ultimately be exhausted. When we apply to the land nitrate of soda, sulphate of ammonia, or guano, we are drawing on the earth's capital, and our drafts will not perpetually be honoured. Already we see that a virgin soil cropped for several years loses its productive powers and without artificial aid becomes infertile. Thus the strain to meet demands is increasingly great. Witness the yield of 40 bushels of wheat per acre under favourable conditions, dwindling through exhaustion of soil to less than 7 bushels of poor grain, and the urgency of husbanding the limited store of fixed nitrogen becomes apparent. The store of nitrogen in the atmosphere is practically unlimited, but it is fixed and rendered assimilable by plants only by cosmic processes of extreme slowness. The nitrogen which with a light heart we liberate in a battleship broadside, has taken millions of minute organisms patiently working for centuries to win from the atmosphere.*

The only available compound containing sufficient fixed nitrogen to be used on a world-wide scale as a nitrogenous manure is nitrate of soda, or Chili saltpetre. This substance occurs native over a narrow band of the plain of Tamarugal, in the northern provinces of Chili between the Andes and the coast hills. In this rainless district for countless ages the continuous fixation of atmospheric nitrogen by the soil, its conversion into nitrate by the slow transformations of billions of nitrifying organisms, its combination with soda, and the crystallisation of the nitrate, have been steadily proceeding until the nitrate fields of Chili have become of vast commercial importance, and promise to be of inestimably greater value in the future. The growing exports of nitrate from Chili at present amount to about 1,200,000 tons.

The present acreage devoted to the world's growth of wheat is about 163,000,000 acres. At the average of 12·7 bushels per acre this gives 2,070,000,000 bushels. But thirty years hence the demand will be 3,260,000,000 bushels, and there will be difficulty in finding the necessary acreage on which to grow the additional amount required. By increasing the present yield per acre from 12·7 to 20 bushels we should with our present acreage secure a crop of the requisite amount. Now from 12·7 to 20 bushels per acre is a moderate increase of productiveness, and there is no doubt that a dressing with nitrate of soda will give this increase and more.

The action of nitrate of soda in improving the yield of wheat has been studied practically by Sir John Lawes and Sir Henry Gilbert on their experimental field at Rothamstead. This field was sown with wheat for thirteen con-

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* Appendix N.

secutive years without manure, and yielded an average of 11·9 bushels to the acre. For the next thirteen years it was sown with wheat, and dressed with 5 cwt. of nitrate of soda per acre, other mineral constituents also being present. The average yield for these years was 36·4 bushels per acre—an increase of 24·5 bushels. In other words 22·86 lbs. of nitrate of soda produce an increase of one bushel of wheat.

At this rate, to increase the world's crop of wheat by 7·3 bushels, about 1½ cwt. of nitrate of soda must annually be applied to each acre. The amount required to raise the world's crop on 163,000,000 acres from the present supply of 2,070,000,000 bushels to the required 3,260,000,000 bushels will be 12 million tons distributed in varying amounts over the wheat-growing countries of the world. The countries which produce more than the average of 12·7 bushels will require less, and those below the average will require more; but broadly speaking, about 12,000,000 tons annually of nitrate of soda will be required, in addition to the 1¼ million tons already absorbed by the world.

It is difficult to get trustworthy estimates of the amount of nitrate surviving in the nitre beds. Common rumour declares the supply to be inexhaustible, but cautious local authorities state that at the present rate of export, of over one million tons per annum, the raw material "caliche," containing from 25 to 50 per cent nitrate, will be exhausted in from twenty to thirty years.

Dr. Newton, who has spent years on the nitrate fields, tells me there is a lower class material containing a small proportion of nitrate which cannot at present be used, but which may ultimately be manufactured at a profit. Apart from a few of the more scientific manufacturers, no one is sanguine enough to think this debatable material will ever be worth working. If we assume a liberal estimate for nitrate obtained from the lower grade deposit, and say that it will equal in quantity that from the richer quality, the supply may last, possibly, fifty years, at the rate of a million tons a year; but at the rate required to augment the world's supply of wheat to the point demanded thirty years hence, it will not last more than four years.

I have passed in review all the wheat-growing countries of the world, with the exception of those whose united supplies are so small as to make little appreciable difference to the argument. The situation may be summed up briefly thus:—The world's demand for wheat—the leading bread-stuff—increases in a crescendo ratio year by year. Gradually all the wheat-bearing land on the globe is appropriated to wheat growing, until we are within measurable distance of using the last available acre. We must then rely on nitrogenous manures to increase the fertility of the land under wheat, so as to raise the yield from the world's low average—12·7 bushels per acre—to a higher average. To do this efficiently and feed the bread-eaters for a few years will exhaust all the available store of nitrate of soda. For years past we have been spending fixed nitrogen at a culpably extravagant rate, heedless of the fact that it is fixed with extreme slowness and difficulty, while its liberation in the free state takes place always with rapidity and sometimes with explosive violence.

Some years ago Mr. Stanley Jevons uttered a note of warning as to the near exhaustion of our British coal fields. But the exhaustion of the world's stock of fixed nitrogen is a matter of far greater importance. It means not only a catastrophe little short of starvation for the wheat-eaters, but indirectly, scarcity for those who exist on inferior grains, together with a lower standard of living for meat eaters, scarcity of mutton and beef, and even the extinction of gunpowder!

There is a gleam of light amid this darkness of despondency. In its free state nitrogen is one of the most abundant and pervading bodies on the face of the earth. Every square yard of the earth's surface has nitrogen gas pressing down on it to the extent of about 7 tons—but this is in the *free* state, and wheat demands it *fixed*. To convey this idea in an object-lesson, I may tell you that, previous to its destruction by fire, Colston Hall, measuring 146 feet by 80 feet by 70 feet, contained 27 tons weight of nitrogen in its atmosphere; it also contained one-third of a ton of argon. In the free gaseous state this nitrogen is worthless; combined in the form of nitrate of soda it would be worth about £2000.

For years past attempts have been made to effect the fixation of atmospheric nitrogen, and some of the processes have met with sufficient partial success to warrant experimentalists in pushing their trials still further; but I think I am right in saying that no process has yet been brought to the notice of scientific or commercial men which can be considered successful either as regards cost or yield of product. It is possible, by several methods, to fix a certain amount of atmospheric nitrogen; but to the best of my knowledge no process has hitherto converted more than a small amount, and this at a cost largely in excess of the present market value of fixed nitrogen.

The fixation of atmospheric nitrogen therefore is one of the great discoveries awaiting the ingenuity of chemists. It is certainly deeply important in its practical bearings on the future welfare and happiness of the civilised races of mankind. This unfulfilled problem, which so far has eluded the strenuous attempts of those who have tried to wrest the secret from nature, differs materially from other chemical discoveries which are in the air, so to speak, but are not yet matured. The fixation of nitrogen is vital to the progress of civilised humanity. Other discoveries minister to our increased intellectual comfort, luxury, or convenience; they serve to make life easier, to hasten the acquisition of wealth, or to save time, health, or worry. The fixation of nitrogen is a question of the not far distant future. Unless we can class it among certainties to come the great Caucasian race will cease to be foremost in the world, and will be squeezed out of existence by races to whom wheaten bread is not the staff of life.

Let me see if it is not possible even now to solve the momentous problem. As far back as 1892 I exhibited at one of the Soirées of the Royal Society an experiment on "The Flame of Burning Nitrogen." I showed that nitrogen is a combustible gas, and the reason why when once ignited the flame does not spread through the atmosphere and deluge the world in a sea of nitric acid is that its igniting point is higher than the temperature of its flame—not, therefore, hot enough to set fire to the adjacent mixture. But by passing a strong induction current between terminals the air takes fire and continues to burn with a powerful flame, producing nitrous and nitric acids. This inconsiderable experiment may not unlikely lead to the development of a mighty industry destined to solve the great food problem. With the object of burning out nitrogen from air so as to leave argon behind, Lord Rayleigh fitted up apparatus for performing the operation on a larger scale, and succeeded in effecting the union of 29·4 grms. of mixed nitrogen and oxygen at an expenditure of one-horse power. Following these figures it would require one Board of Trade unit to form 74 grms. of nitrate of soda, and therefore 14,000 units to form one ton. To generate electricity in the ordinary way with steam engines and dynamos, it is now possible with a steady load night and day, and engines working at maximum efficiency, to produce current at a cost of one-third of a penny per Board of Trade unit. At this rate one ton of nitrate of soda would cost £26. But electricity from coal and steam engines is too costly for large industrial purposes; at Niagara where water power is used, electricity can be sold at a profit for 1/17th of a penny per Board of Trade unit. At this rate nitrate of soda would cost not more than £5 per ton. But the limit of cost is not yet reached, and it must be remembered that the initial data are derived from small scale experiments, in which the object was not economy, but rather to demonstrate the practicability of the combustion method, and to utilise it for isolating argon. Even now electric nitrate at £5 a ton compares favourably with

Chili nitrate at £7 10s. a ton; and all experience shows that when the road has been pointed out by a small laboratory experiment the industrial operations that may follow are always conducted at a cost considerably lower than could be anticipated from the laboratory figures.

Before we decide that electric nitrate is a commercial possibility a final question must be mooted. We are dealing with wholesale figures, and must take care that we are not simply shifting difficulties a little further back without really diminishing them. We start with a shortage of wheat, and the natural remedy is to put more land under cultivation. As the land cannot be stretched and there is so much of it and no more, the object is to render the available area more productive by a dressing with nitrate of soda. But nitrate of soda is limited in quantity, and will soon be exhausted. Human ingenuity can contend even with these apparently hopeless difficulties. Nitrate can be produced artificially by the combustion of the atmosphere. Here we come to finality in one direction, our stores are inexhaustible. But how about electricity? Can we generate enough energy to produce 12,000,000 tons of nitrate of soda annually. A preliminary calculation shows that there need be no fear on that score; Niagara alone is capable of supplying the required electric energy without much lessening its mighty flow.

The future can take care of itself. The artificial production of nitrate is clearly within view, and by its aid the land devoted to wheat can be brought up to the 30 bushels per acre standard. In days to come, when the demand may again overtake supply, we may safely leave our successors to grapple with the stupendous food problem.

And in the next generation instead of trusting mainly to food-stuffs which flourish in temperate climates, we probably shall trust more and more to the exuberant food-stuffs of the tropics, where, instead of one yearly sober harvest, jeopardised by any shrinkage of the scanty days of summer weather, or of the few steady inches of rainfall, Nature annually supplies heat and water enough to ripen two or three successive crops of food-stuffs in extraordinary abundance. To mention one plant alone, Humboldt—from what precise statistics I know not—computed that, acre for acre, the food-productiveness of the banana is 133 times that of wheat—the unripe banana, before its starch is converted into sugar, is said to make excellent bread.

Considerations like these must in the end determine the range and avenues of commerce, perhaps the fate of continents. We must develope and guide Nature's latent energies, we must utilise her inmost workshops, we must call into commercial existence Central Africa and Brazil to redress the balance of Odessa and Chicago.

Having kept you for the last half-hour rigorously chained to earth, disclosing dreary possibilities, it will be a relief to soar to the heights of pure Science and to discuss a point or two touching its latest achievements and aspirations. The low temperature researches which bring such renown to Professor Dewar and to his laboratory in the Royal Institution, have been crowned during the present year by the conquest of one of Nature's most defiant strongholds. On the 10th of last May Professor Dewar wrote to me these simple but victorious words—"This evening I have succeeded in liquefying both hydrogen and helium. The second stage of low temperature work has begun." Static hydrogen boils at a temperature of −238° C. at ordinary pressure, and at −250° C. in a vacuum, thus enabling us to get within 23° C. of absolute zero. The density of liquid hydrogen is only 1/14th that of water, yet in spite of such a low density it collects well, drops easily, and has a well-defined meniscus. With proper isolation it will be as easy to manipulate liquid hydrogen as liquid air.

The investigation of the properties of bodies brought near the absolute zero of temperature is certain to give results of extraordinary importance. Already platinum resistance thermometers are becoming useless, as the temperature of boiling hydrogen is but a few degrees from the point where the resistance of platinum would be practically nothing, or the conductivity infinite.

Several years ago I pondered on the constitution of matter in what I ventured to call the fourth state. I endeavoured to probe the tormenting mystery of the atom. What *is* the atom? Is a single atom in space solid, liquid, or gaseous? Each of these states involves ideas which can only pertain to vast collections of atoms. Whether like Newton, we try to visualise an atom as a hard spherical body, or with Boscovitch and Faraday, to regard it as a centre of force, or accept the vortex atom theory of Lord Kelvin, an isolated atom is an unknown entity difficult to conceive. The properties of matter—solid, liquid, gaseous—are due to molecules in a state of motion. Therefore, Matter as we know it involves essentially a mode of motion; and the atom itself—intangible, invisible, and inconceivable—is its material basis, and may, indeed, be styled the only true *matter.* The space involved in the motions of atoms has no more pretension to be called matter than the sphere of influence of a body of riflemen—the sphere filled with flying leaden missiles—has to be called lead. Since what we call Matter essentially involves a mode of motion, and since at the temperature of absolute zero all atomic motions would stop, it follows that matter as we know it would at that paralysing temperature probably entirely change its properties. Although a discussion of the ultimate absolute properties of matter is purely speculative, it can hardly be barren, considering that in our laboratories we are now within moderate distance of the absolute zero of temperature.

I have dwelt on the value and importance of nitrogen, but I must not omit to bring to your notice those little known and curiously related elements which during the past twelve months have been discovered and partly described by Professor Ramsay and Dr. Travers. For many years my own work has been among what I may call the waste heaps of the mineral elements. Professor Ramsay is dealing with vagrant atoms of an astral nature. During the course of the present year he has announced the existence of no fewer than three new gases—krypton, neon, and metargon. Whether these gases, chiefly known by their spectra, are true unalterable elements, or whether they are compounded of other known or unknown bodies, has yet to be proved. Fellow workers freely pay tribute to the painstaking zeal with which Professor Ramsay has conducted a difficult research, and to the philosophic subtlety brought to bear on his investigations. But, like most discoverers, he has not escaped the flail of severe criticism.

There is still another claimant for celestial honours. Professor Nasini tells us he has discovered, in some volcanic gases at Pozzuoli, that hypothetical element Coronium, supposed to cause the bright line 5316·9 in the spectrum of the sun's corona. Analogy points to its being lighter and more diffusible than hydrogen, and a study of its properties cannot fail to yield striking results. Still awaiting discovery by the fortunate spectroscopist are the unknown celestial elements Aurorium, with a characteristic line at 5570·7—and Nebulum, having two bright lines at 5007·05 and 4959·02.

The fundamental discovery by Hertz, of the electromagnetic waves predicted more than thirty years ago by Clerk Maxwell, seems likely to develop in the direction of a practical application which excites keen interest;—I mean the application to electric signalling across moderate distances without connecting wires. The feasibility of this method of signalling has been demonstrated by several experimenters at more than one meeting of the British Association, though most elaborately and with many optical refinements by Oliver Lodge at the Oxford meeting in 1894. But not until Signor Marconi induced the British Post-Office and Foreign Governments to try large scale experiments did wireless signalling become generally and popularly known or practically developed as a special kind of telegraphy. Its feasibility depends on the discovery of a singularly sensitive detector for Hertz waves,—a detector whose sensitiveness in some cases seems almost to compare with that of the eye itself. The fact noticed by Oliver Lodge in 1889, that an infinitesimal metallic gap subjected to an electric jerk became conducting, so as to complete an electric circuit, was re-discovered soon afterwards in a more tangible and definite form and applied to the detection of Hertz waves by M. E. Branly. Oliver Lodge then continued the work and produced the *vacuum filing-tube* coherers with automatic tapperback which are of acknowledged practical service. It is this varying continuity of contact under the influence of extremely feeble electric stimulus alternating with mechanical tremor, which, in combination with the mode of producing the waves revealed by Hertz, constitutes the essential and fundamental feature of "wireless telegraphy." There is a curious and widely spread misapprehension about coherers to the effect that to make a coherer work the wave must fall upon it. Oliver Lodge has disproved this fallacy. Let the wave fall on a suitable receiver, such as a metallic wire, or, better still, on an arrangement of metal wings resembling a Hertz sender, and the waves set up oscillating currents which may be led by wires (enclosed in metal pipes) to the coherer. The coherer acts apparently by a species of end-impact of the oscillatory current, and does not need to be attacked in the flank by the waves themselves. This interesting method of signalling — already developing in Marconi's hands into a successful practical system which inevitably will be largely used in lighthouse and marine work — presents more analogy to optical signals by flash-light than to what is usually understood as electric telegraphy; notwithstanding the fact that an ordinary Morse instrument at one end responds to the movements of a key at the other, or, as arranged by Alexander Muirhead, a siphon recorder responds to an automatic transmitter at about the rate of slow cable telegraphy. But although no apparent optical apparatus is employed, it remains true that the impulse travels from sender to receiver by essentially the same process as that which enables a flash of magnesium powder to excite a distant eye.

The phenomenon discovered by Zeeman, that a source of radiation is affected by a strong magnetic field in such a way that light of one refrangibility becomes divided usually into three components, two of which are displaced by diffraction analysis on either side of the mean position and are oppositely polarised to the third or residual constituent, has been examined by many observers in all countries. The phenomenon has been subjected to photography with conspicuously successful results by Professor T. Preston in Dublin and by Professor Michelson and Dr. Ames and others in America.

It appears that the different lines in the spectrum are differently affected, some of them being tripled with different grades of relative intensity, some doubled, some quadrupled, some sextupled, and some left unchanged. Even the two components of the D lines are not similarly influenced. Moreover, whereas the polarisation is usually such as to indicate that motions of a negative ion or electron constitute the source of light, a few lines are stated by the observers at Baltimore, who use what they call the "small" grating of 5 inches width ruled with 65,000 lines, to be polarised in the reverse way.

Further prosecution of these researches must lead to deeper insight into molecular processes and the mode in which they affect the ether; indeed already valuable theoretic views have been promulgated by H. A. Lorentz, J. Larmor, and G. F. Fitzgerald, on the lines of the radiation theory of Dr. Johnstone Stoney; and the connection of the new phenomena with the old magnetic rotation of Faraday is under discussion. It is interesting to note that Faraday and a number of more recent experimenters were led by theoretical considerations to look for some such effect; and though the inadequate means at their disposal did not lead to success, nevertheless a first dim glimpse of the phenomenon was obtained by M. Fievez, of the Royal Observatory at Brussels, in 1885.

It would be improper to pass without at least brief mention, the remarkable series of theoretic papers by Dr. J. Larmor, published by the Royal Society, on the relationship between ether and matter. By the time these researches become generally intelligible they may be found to constitute a considerable step towards the further mathematical analysis and interpretation of the physical universe on the lines initiated by Newton.

In the mechanical construction of Röntgen ray tubes I can record a few advances: the most successful being the adoption of Professor Silvanus P. Thompson's suggestion of using for the anti-cathode a metal of high atomic weight. Osmium and iridium have been used with advantage, and osmium anticathode tubes are now a regular article of manufacture. As long ago as June, 1896, X-ray tubes with metallic uranium anticathodes were made in my own laboratory, and were found to work better than those with platinum. The difficulty of procuring metallic uranium prevented these experiments from being continued. Thorium anticathodes have also been tried.

Röntgen has drawn fresh attention to a fact very early observed by English experimenters — that of the non-homogeneity of the rays and the dependence of their penetrating power on the degree of vacuum; rays generated in high vacua have more penetrative power than when the vacuum is less high. These facts are familiar to all who have exhausted focus tubes on their own pumps. Röntgen suggests a convenient phraseology; he calls a low vacuum tube, which does not emit the highly penetrating rays, a "soft" tube, and a tube in which the exhaustion has been pushed to an extreme degree, in which highly penetrating rays predominate, a "hard" tube. Using a "hard" tube he took a photograph of a double-barrelled rifle, and showed not only the leaden bullets within the steel barrels but even the wads and the charges.

Benoit has re-examinnd the alleged relation between density and opacity to the rays, and finds certain discrepancies. Thus, the opacity of equal thicknesses of palladium and platinum are nearly equal whilst their densities and atomic weights are very different, those of palladium being about half those of platinum.

At the last meeting of the British Association visitors saw — at the McGill University — Professors Cox and Callendar's apparatus for measuring the velocity of Röntgen rays. They found it to be certainly greater than 200 kilometres per second. Majorana has made an independent determination, and finds the velocity to be 600 kilometres per second with an inferior limit certainly of not less than 150 kilometres per second. It may be remembered that J. J. Thomson has found for cathode rays a velocity of more than 10,000 kilometres per second, and it is extremely unlikely that the velocity of Röntgen rays will prove to be less.

Trowbridge has verified the fact, previously announced by Professor S. P. Thompson, that fluor-spar, which by prolonged heating has lost its power of luminescing when re-heated, regains the power of thermo-luminescence when exposed to Röntgen rays. He finds that this restoration is also effected by exposure to the electric glow discharge, but not by exposure to ultra-violet light. The difference is suggestive.

As for the action of Röntgen rays on bacteria, often asserted and often denied, the latest statement by Dr. H. Rieder, of Munich, is to the effect that bacteria are killed by the discharge from "hard" tubes. Whether the observation will lead to results of pathologic importance remains to be seen. The circumstance that the normal retina of the eye is slightly sensitive to the rays is confirmed by Dorn and by Röntgen himself.

The essential wave-nature of the Röntgen rays appears to be confirmed by the fact ascertained by several of our great mathematical physicists, that light of excessively short wave-length would be but slightly absorbed by ordinary material media, and would not in the ordinary sense be refracted at all. In fact a theoretic basis for a comprehension of the Röntgen rays had been propounded before the rays were discovered. At the Liverpool meeting of the British Association, several speakers, headed by Sir George Stokes, expressed their conviction that the disturbed electric field caused by the sudden stoppage of the motion of an electrically charged atom yielded the true explanation of the phenomena extraneous to the Crookes high vacuum tubes,—phenomena so excellently elaborated by Lenard and by Röntgen. More recently Sir George Stokes has re-stated his "pulse" theory and fortified it with arguments which have an important bearing on the whole theory of the refraction of light. He still holds to their essentially transverse nature, in spite of the absence of polarisation, an absence once more confirmed by the careful experiments of Dr. L. Graetz. The details of this theory are in process of elaboration by Professor J. J. Thomson.

Meantime, while the general opinion of physicists seems to be settling towards a wave or ether theory for the Röntgen rays, an opposite drift is apparent with respect to the physical nature of the cathode rays: it becomes more and more clear that cathode rays consist of electrified atoms or ions in rapid progressive motion. My idea of a fourth state of matter, propounded in 1881,* and at first opposed at home and abroad, is now becoming accepted. It is supported by Professor J. J. Thomson:† Dr. Larmor's theory‡ likewise involves the idea of an ionic substratum of matter; the view is also confirmed by Zeeman's phenomenon. In Germany, where the term cathode ray was invented almost as a protest against the theory of molecular streams propounded by me at the Sheffield meeting of the British Association in 1879, additional proofs have been produced in favour of the doctrine that the essential fact in the phenomenon is electrified Radiant Matter.

The speed of these molecular streams has been approximately measured, chiefly by aid of my own discovery nearly twenty years ago, that their path is curved in a magnetic field and that they produce phosphorescence where they impinge on an obstacle. The two unknown quantities, the charge and the speed of each atom, are measurable from the amount of curvature and by means of one other independent experiment.

It cannot be said that a complete and conclusive theory of these rays has yet been formulated. It is generally accepted that collisions among particles, especially the violent collisions due to their impact on a massive target placed in their path, give rise to the interesting kind of extremely high frequency radiation discovered by Röntgen. It has indeed for some time been known that whereas a charged body in motion constitutes an electric current, the sudden stoppage, or any violent acceleration of such a body, must cause an alternating electric disturbance, which though so rapidly decaying in intensity as to be practically "dead beat," yet must give rise to an ethereal wave or pulse travelling with the speed of light but of a length comparable to the size of the body whose sudden change of motion caused the disturbance. The emission of a high-pitched musical sound from the jolting of a dustman's cart (with a spring bell hung on it) has been suggested as an illustration of the way in which the molecules of any solid not at absolute zero may possibly emit such rays.

If the target on to which the electrically charged atoms impinge is so constituted that some of its minute parts can thereby be set into rhythmical vibration, the energy thus absorbed reappears in the form of light and the body is said to phosphoresce. The efficient action of the phosphorescent target appears to depend as much on its physical and molecular as on its chemical constitution. The best known phosphori belong to certain well-defined classes, such as the sulphides of the alkaline-earthy metals, and some of the so-called rare earths; but the phosphorescent properties of each of these groups are profoundly modified by an admixture of foreign bodies—witness the effect on the lines in the phosphorescent spectrum of yttrium and samarium produced by traces of calcium or lead. The persistence of the samarium spectrum in presence of overwhelming quantities of other metals is almost unexampled in spectroscopy: thus one part of samaria can easily be seen when mixed with three million parts of lime.

Without stating it as a general rule it seems as if with a non-phosphorescing target the energy of molecular impact reappears as pulses so abrupt and irregular that when resolved they furnish a copious supply of waves of excessively short wave-length, in fact the now well-known Röntgen rays. The phosphorescence so excited may last only a small fraction of a second, as with the constituents of yttria, where the duration of the different lines varies between the 0·003 and the 0·0009 second; or it may linger for hours, as in the case of some of the yttria earths, and especially with the earthy sulphides, where the glow lasts bright enough to be commercially useful. Excessively phosphorescent bodies can be excited by light waves, but most of them require the stimulus of electrical excitement.

It now appears that some bodies, even without special stimulation, are capable of giving out rays closely allied if not in some cases identical with those of Professor Röntgen. Uranium and thorium compounds are of this character, and it would almost seem from the important researches of Dr. Russell, that this ray-emitting power may be a general property of matter, for he has shown that nearly every substance is capable of affecting the photographic plate if exposed in darkness for sufficient time.

No other source for Röntgen rays but the Crookes tube has yet been discovered, but rays of kindred sorts are recognised. The Becquerel rays, emitted by uranium and its compounds, have now found their companions in rays—discovered almost simultaneously by Curie and Schmidt—emitted by thorium and its compounds. The thorium rays affect photographic plates through screens of paper or aluminium and are absorbed by metals and other dense bodies. They ionise the air, making it an electrical conductor; and they can be refracted and probably reflected, at least diffusively. Unlike uranium rays, they are not polarised by transmission through tourmaline, therefore resembling in this respect the Röntgen rays.

Quite recently M. and Mdme. Curie have announced a discovery which if confirmed cannot fail to assist the investigation of this obscure branch of physics. They have brought to notice a new constituent of the uranium mineral pitchblende, which in a 400-fold degree possesses Uranium's mysterious power of emitting a form of energy capable of impressing a photographic plate and of discharging electricity by rendering air a conductor. It also appears that the radiant activity of the new body, to which the discoverers have given the name of Polonium, needs neither the excitation of light nor the stimulus of electricity; like uranium, it draws its energy from some constantly regenerating and hitherto unsuspected store, exhaustless in amount.

It has long been to me a haunting problem how to reconcile this apparently boundless out-pour of energy with accepted canons. But as Dr. Johnstone Stoney reminds me, the resources of molecular movements are far from exhausted. There are many stores of energy in Nature that may be drawn on by properly constituted bodies without very obvious cause. Some time since I drew attention to the enormous amount of locked up energy in the ether; nearer our experimental grasp are the motions of atoms and molecules, and it is not difficult mentally so to modify Maxwell's demons as to reduce

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* *Phil. Tranz.*, Part 2, 1881, pp. 433-4.

† *Phil. Mag.*, October, 1897, p. 312.

‡ *Phil. Mag.*, December, 1897, p. 506.

them to the level of an inflexible law and thus bring them within the ken of a philosopher in search of a new tool. It is possible to conceive a target capable of mechanically sifting from the molecules of the surrounding air the quick from the slow movers. This sifting of the swift moving molecules is effected in liquids whenever they evaporate, and in the case of the constituents of the atmosphere, wherever it contains constituents light enough to drift away molecule by molecule. In my mind's eye I see such a target as a piece of metal cooler than the surrounding air acquiring the energy that gradually raises its temperature from the outstanding effect of all its encounters with the molecules of the air about it; I see another target of such a structure that it throws off the slow moving molecules with little exchange of energy, but is so influenced by the quick moving missiles that it appropriates to itself some of their energy. Let uranium or polonium, bodies of densest atoms, have a structure that enables them to throw off the slow moving molecules of the atmosphere, while the quick moving molecules, smashing on to the surface, have their energy reduced and that of the target correspondingly increased. The energy thus gained seems to be employed partly in dissociating some of the molecules of the gas (or in inducing some other condition which has the effect of rendering the neighbouring air in some degree a conductor of electricity) and partly in originating an undulation through the ether, which, as it takes its rise in phenomena so disconnected as the impacts of the molecules of the air, must furnish a large contingent of light waves of short wave-length. The shortness in the case of these Becquerel rays appears to approach without attaining the extreme shortness of ordinary Röntgen rays. The reduction of the speed of the quick moving molecules would cool the layer of air to which they belong; but this cooling would rapidly be compensated by radiation and conduction from the surrounding atmosphere: under ordinary circumstances the difference of temperature would scarcely be perceptible and the uranium would thus appear to perpetually emit rays of energy with no apparent means of restoration.

The total energy of both the translational and internal motions of the molecules locked up in quiescent air at ordinary pressure and temperature is about 140,000 foot-pounds in each cubic yard of air. Accordingly the quiet air within a room 12 feet high, 18 feet wide, and 22 feet long, contains energy enough to propel a one-horse engine for more than twelve hours. The store drawn upon naturally by uranium and other heavy atoms only awaits the touch of the magic wand of Science to enable the Twentieth Century to cast into the shade the marvels of the Nineteenth.

Whilst placing before you the labours and achievements of my comrades in Science I seize this chance of telling you of engrossing work of my own on the fractionation of yttria, to which for the last eighteen years I have given ceaseless attention. In 1883, under the title of "Radiant Matter Spectroscopy," I described a new series of spectra produced by passing the phosphorescent glow of yttria, under molecular bombardment *in vacuo*, through a train of prisms. The visible spectra in time gave up their secrets, and were duly embalmed in the *Philosophical Transactions.* At the Birmingham Meeting of the British Association in 1886 I brought the subject before the Chemical Section, of which I had the honour to be President. The results led to many speculations on the probable origin of all the elementary bodies—speculations that for the moment I must waive in favour of experimental facts.

There still remained for spectroscopic examination a long tempting stretch of unknown ultra-violet light, of which the exploration gave me no rest. But I will not now enter into details of the quest of unknown lines. Large quartz prisms, lenses, and condensers, specially sensitised photographic films capable of dealing with the necessary small amount of radiation given by feebly phosphorescing substances,* and above all tireless patience in collating and interpreting results, have all played their part. Although the research is incomplete I am able to announce that among the groups of rare earths giving phosphorescent spectra in the visible region there are others giving well-defined groups of bands which can only be recorded photographically. I have detected and mapped no less than six such groups extending to λ 3060.

Without enlarging on difficulties, I will give a brief outline of the investigation. Starting with a large quantity of a group of the rare earths in a state of considerable purity, a particular method of fractionation is applied, splitting the earths into a series of fractions differing but slightly from each other. Each of these fractions, phosphorescing *in vacuo*, is arranged in the spectrograph, and a record of its spectrum photographed upon a specially prepared sensitive film.

In this way, with different groups of rare earths, the several invisible bands were recorded—some moderately strong, others exceedingly faint. Selecting a portion giving a definite set of bands, new methods of fractionation were applied, constantly photographing and measuring the spectrum of each fraction. Sometimes many weeks of hard experiment failed to produce any separation, and then a new method of splitting up was devised and applied. By unremitting work—the solvent of most difficulties—eventually it was possible to split up the series of bands into various groups. Then, taking a group which seemed to offer possibilities of reasonably quick result, one method after another of chemical attack was adopted, with the ultimate result of freeing the group from its accompanying fellows and increasing its intensity and detail.

As I have said, my researches are far from complete, but about one of the bodies I may speak definitely. High up in the ultra-violet, like a faint nebula in the distant heavens, a group of lines was detected, at first feeble and only remarkable on account of their isolation. On further purification these lines grew stronger. Their great refrangibility cut them off from other groups. Special processes were employed to isolate the earth, and using these lines as a test, and appealing at every step to the spectrograph, it was pleasant to see how each week the group stood out stronger and stronger, while the other lines of yttrium, samarium, ytterbium, &c., became fainter, and at last practically vanishing left the sought for group strong and solitary. Finally, within the last few weeks, hopefulness has merged into certainty, and I have absolute evidence that another member of the rare earth groups has been added to the list. Simultaneously with the chemical and spectrographic attack, atomic weight determinations were constantly performed.

As the group of lines which betrayed its existence stand alone, almost at the extreme end of the ultra-violet spectrum, I propose to name the newest of the elements Monium, from the Greek *μόνος*, alone. Although caught by the searching rays of the spectrum, Monium offers a direct contrast to the recently discovered gaseous elements, by having a strongly marked individuality; but although so young and wilful, it is willing to enter into any number of chemical alliances.

Until my material is in a greater state of purity I hesitate to commit myself to figures; but I may say that the wave-lengths of the principal lines are 3120 and 3117. Other fainter lines are at 3219, 3064, and 3060. The atomic weight of the element, based on the assumption of R_2O_3, is not far from 118,—greater than that accepted for yttrium and less than that for lanthanum.

I ought almost to apologise for adding to the already too long list of elements of the rare earth class,—the asteroids of the terrestrial family. But as the host of

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* In this direction I am glad to acknowledge my indebtedess to Dr. Schumann, of Leipzig, for valuable suggestions and details of his own apparatus, by means of which he has produced some unique records of metallic and gaseous spectra of lines of short wave-length.

celestial asteroids, unimportant individually, become of high interest when once the idea is grasped that they may be incompletely coagulated remains of the original nebula, so do these elusive and insignificant rare elements rise to supreme importance when we regard them in the light of component parts of a dominant element, frozen in embryo, and arrested in the act of coalescing from the original protyle into one of the orderly and law abiding family for whom Newlands and Mendeleeff have prepared pigeon-holes. The new element has another claim to notice. Not only is it new in itself, but to discover it a new tool had to be forged for spectroscopic research.

Further details I will reserve for that tribunal before whom every aspirant for a place in the elemental hierarchy has to substantiate his claim.

These, then, are some of the subjects, weighty and far-reaching, on which my own attention has been chiefly concentrated. Upon one other interest I have not yet touched—to me the weightiest and the farthest reaching of all.

No incident in my scientific career is more widely known than the part I took many years ago in certain psychic researches. Thirty years have passed since I published an account of experiments tending to show that outside our scientific knowledge there exists a Force exercised by intelligence differing from the ordinary intelligence common to mortals. This fact in my life is of course well understood by those who honoured me with the invitation to become your President. Perhaps among my audience some may feel curious as to whether I shall speak out or be silent. I elect to speak, although briefly. To enter at length on a still debatable subject would be unduly to insist on a topic which,—as Wallace, Lodge, and Barrett have already shown,—though not unfitted for discussion at these meetings, does not yet enlist the interest of the majority of my scientific brethren. To ignore the subject would be an act of cowardice—an act of cowardice I feel no temptation to commit.

To stop short in any research that bids fair to widen the gates of knowledge, to recoil from fear of difficulty or adverse criticism, is to bring reproach on Science. There is nothing for the investigator to do but to go straight on, "to explore up and down, inch by inch, with the taper his reason;" to follow the light wherever it may lead, even should it at times resemble a will-o'-the wisp. I have nothing to retract. I adhere to my already published statements. Indeed, I might add much thereto. I regret only a certain crudity in those early expositions which, no doubt justly, militated against their acceptance by the scientific world. My own knowledge at that time scarcely extended beyond the fact that certain phenomena new to science had assuredly occurred, and were attested by my own sober senses, and better still, by automatic record. I was like some two-dimensional being who might stand at the singular point of a Riemann's surface, and thus find himself in infinitesimal and inexplicable contact with a plane of existence not his own.

I think I see a little farther now. I have glimpses of something like coherence among the strange elusive phenomena; of something like continuity between those unexplained forces and laws already known. This advance is largely due to the labours of another Association of which I have also this year the honour to be President—the Society for Psychical Research. And were I now introducing for the first time these inquiries to the world of science I should choose a starting-point different from that of old. It would be well to begin with *telepathy;* with the fundamental law, as I believe it to be, that thoughts and images may be transferred from one mind to another without the agency of the recognised organs of sense—that knowledge may enter the human mind without being communicated in any hitherto known or recognised ways.

Although the enquiry has elicited important facts with reference to the Mind, it has not yet reached the scientific stage of certainty which would entitle it to be usefully brought before one of our Sections. I will therefore confine myself to pointing out the direction in which scientific investigation can legitimately advance. If telepathy take place we have two physical facts—the physical change in the brain of A, the suggester, and the analogous physical change in the brain of B, the recipient of the suggestion. Between these two physical events there must exist a train of physical causes. Whenever the connecting sequence of intermediate causes begins to be revealed the enquiry will then come within the range of one of the Sections of the British Association. Such a sequence can only occur through an intervening medium. All the phenomena of the universe are presumably in some way continuous, and it is unscientific to call in the aid of mysterious agencies when with every fresh advance in knowledge it is shown that ether vibrations have powers and attributes abundantly equal to any demand—even to the transmission of thought. It is supposed by some physiologists that the essential cells of nerves do not actually touch, but are separated by a narrow gap which widens in sleep, while it narrows almost to extinction during mental activity. This condition is so singularly like that of a Branly or Lodge coherer as to suggest a further analogy. The structure of brain and nerve being similar, it is conceivable there may be present masses of such nerve coherers in the brain whose special function it may be to receive impulses brought from without through the connecting sequence of ether waves of appropriate order of magnitude. Röntgen has familarised us with an order of vibrations of extreme minuteness compared with the smallest waves with which we have hitherto been acquainted, and of dimensions comparable with the distances between the centres of the atoms of which the material universe is built up; and there is no reason to suppose that we have here reached the limit of frequency. It is known that the action of thought is accompanied by certain molecular movements in the brain, and here we have physical vibrations capable from their extreme minuteness of acting direct on individual molecules, while their rapidity approaches that of the internal and external movements of the atoms themselves.

Confirmation of telepathic phenomena is afforded by many converging experiments, and by many spontaneous occurrences only thus intelligible. The most varied proof, perhaps, is drawn from analysis of the sub-conscious workings of the mind, when these, whether by accident or design, are brought into conscious survey. Evidence of a region, below the threshold of consciousness, has been presented, since its first inception, in the *Proceedings of the Society for Psychical Research;* and its various aspects are being interpreted and welded into a comprehensive whole by the pertinacious genius of F. W. H. Myers. Concurrently, our knowledge of the facts in this obscure region has received valuable additions at the hands of labourers in other countries. To mention a few names out of many, the observations of Richet, Pierre Janet, and Binet (in France), of Breuer and Freud (in Austria), of William James (in America) have strikingly illustrated the extent to which patient experimentation can probe sub-liminal processes, and can thus learn the lessons of alternating personalities and abnormal states. Whilst it is clear that our knowledge of sub-conscious mentation is still to be developed we must beware of rashly assuming that all variations from the normal waking condition are necessarily morbid. The human race has reached no fixed or changeless ideal: in every direction there is evolution as well as disintegration. It would be hard to find instances of more rapid progress, moral and physical, than in certain important cases of cure by suggestion—again to cite a few names out of many—by Liébault, Bernheim, the late Auguste Voisin, Bérillon (in France), Schrenck-Notzing (in Germany), Forel (in Switzerland), van Eeden (in Holland), Wetterstrand (in Sweden), Milne-Bramwell and Lloyd Tuckey (in England). This is not the place for details, but the *vis* *medicatrix* thus evoked, as it were, from the depths of the organism, is of good omen for the upward evolution of mankind.

A formidable range of phenomena must be scientifically sifted before we effectually grasp a faculty so strange, so bewildering, and for ages so inscrutable, as the direct action of mind on mind. This delicate task needs a rigorous employment of the method of exclusion—a constant setting aside of irrelevant phenomena that could be explained by known causes, including those far too familiar causes, conscious and unconscious fraud. The enquiry unites the difficulties inherent in all experimentation connected with *mind*, with tangled human temperaments and with observations dependent less on automatic record than on personal testimony. But difficulties are things to be overcome even in the elusory branch of research known as Experimental Psychology.

It has been characteristic of the leaders among the group of enquirers constituting the Society for Psychical Research to combine critical and negative work with work leading to positive discovery. To the penetration and scrupulous fairmindedness of Professor Henry Sidgwick and of the late Edmund Gurney is largely due the establishment of canons of evidence in psychical research, which strengthen while they narrow the path of subsequent explorers. To the detective genius of Dr. Richard Hodgson we owe a convincing demonstration of the narrow limits of human continuous observation.

It has been said that "Nothing worth the proving can be proved, nor yet dis-proved." True though this may have been in the past, it is true no longer. The Science of our century has forged weapons of observation and analysis by which the veriest tyro may profit. Science has trained and fashioned the average mind into habits of exactitude and disciplined perception, and in so doing has fortified itself for tasks higher, wider, and incomparably more wonderful than even the wisest among our ancestors imagined. Like the souls in Plato's myth that follow the chariot of Zeus, it has ascended to a point of vision far above the earth. It is, henceforth, open to Science to transcend all we now think we know of matter, and to gain new glimpses of a profounder scheme of Cosmic Law.

An eminent predecessor in this Chair declared that "by an intellectual necessity he crossed the boundary of experimental evidence, and discerned in that Matter, which we in our ignorance of its latent powers, and notwithstanding our professed reverence for its Creator, have hitherto covered with opprobrium, the potency and promise of all terrestrial life." I should prefer to reverse the apophthegm, and to say that in Life I see the promise and potency of all forms of Matter.

In old Egyptian days a well known inscription was carved over the portal of the temple of Isis:—"I am whatever hath been, is, or ever will be; and my veil no man hath yet lifted." Not thus do modern seekers after truth confront Nature—the word that stands for the baffling mysteries of the Universe. Steadily, unflinchingly, we strive to pierce the inmost heart of Nature, from what she is to re-construct what she has been, and to prophesy what she yet shall be. Veil after veil we have lifted, and her face grows more beautiful, august, and wonderful, with every barrier that is withdrawn.

(To be continued).

Allen's Commercial Organic Analysis.—We are glad to learn that the second edition of this well-known work is very near its completion. Its publishers, Messrs. J. and A. Churchill, announce the fourth (concluding) volume for issue in October. The first two volumes and the first part of the third have long been out of print, and second-hand copies have commanded a high price. The author, not being at present able to revise these as he would like, has willingly accepted the aid of Dr. Henry Leffmann, of Philadelphia, in making such addenda and editorial notes as are necessary to bring them in many important particulars up to date. Messrs. Churchill will publish Vol. I. almost immediately, and the other two will follow at no distant date.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JULY 31ST, 1898.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To Major-General A. De Courcy Scott, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, August 10th, 1898.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from July 1st to July 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined by us during the month, one was found to be clear but dull, all the rest being clear, bright, and well filtered.

We have this month to record a very serious deficiency in the rainfall at Oxford. The actual amount which fell was but 0·53 inch. The average July fall for the past thirty years is 2·68 inches, leaving a deficiency of 2·15 inches. On the 1st July 0·22 inch of rain fell; rain also fell on five other days, but never so much as a tenth of an inch. The total deficiency for the year is now 5·49 inches.

Our bacteriological examinations of 258 samples have given the results recorded in the following table; we have also examined 39 other samples, from special wells, standpipes, &c., making a total of 297 samples in all:—

		Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..		358
New River, filtered (mean of 26 samples) ..		12
Thames, unfiltered (mean of 26 samples) ..		1132
Thames water, from the clear water wells of five Thames-derived supplies (mean of 128 samples)		40
Ditto ditto	highest	682
Ditto ditto	lowest	0
River Lea, unfiltered (mean of 26 samples) ..		3080
River Lea, from the East London Company's clear water well (mean of 26 samples) . ..		35

The quality of the water supplied to the Metropolis during the month of July has been very similar to that of last month, and is of excellent character both in colour and in freedom from organic impurity.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

NOTES AND QUERIES.

. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Gasoline.—A correspondent wishes to know how gasoline is manufactured.

THE CHEMICAL NEWS.

Vol. LXXVIII., No. 2025.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

BRISTOL, 1898.

INAUGURAL ADDRESS OF THE PRESIDENT,

SIR WILLIAM CROOKES, F.R.S., V.P.C.S.

(Concluded from p. 135).

APPENDIX.

In preparing the part of this address dealing with the world's supply and demand for wheat, and the conclusions based thereon, I have been materially assisted by Mr. C. Wood Davis, of Kansas, U.S.A. Apart from information obtained from Mr. Davis's articles in *The Forum*, the *North-Western Miller*, the *New York Sun*, and other papers, I am indebted to him for valuable manuscript information on matters of detail. Mr. Davis appears to be the only person dealing with this problem in a manner to determine such essential factors as average acre yields for long periods, unit requirements for each of the primary food staples of the temperate zones, and the ratios existing during different recent periods between the consuming element and acres employed in the production of each of such primary food staples. His scientific method enables him to ascertain the acreage requirements of the separate national populations, and of the "bread-eating" world as a whole. Information has also been obtained from the "Agricultural Returns of the United Kingdom," the official "Reports on Agricultural Depression," and the Annual Reports of the United States Secretary of Agriculture; likewise from papers and articles by Sir John Lawes, Sir H. Gilbert, Major Craigie, Mr. W. E. Bear, Mr. Warington, Professor E. M. Shelton, Mr. R. F. Crawford, Dr. Newton, and Mr. W. Walgrave Chapman. The *Journal of the Royal Agricultural Society*, the *Journal of the Royal Statistical Society*, the *Journal of the Board of Agriculture*, and other periodicals have also been laid under contribution. I am also indebted to the various official publications of the Government of Canada, the Department of Agriculture, Queensland, and to friends all over the world.

A.

Last year there were under corn crops in the United Kingdom:—

Wheat ..	3025 sq. miles,	producing 56,296,000 bushels.
Barley ..	3447 "	
Oats . ..	6580 "	
Total ..	13,052 "	

There is now about as much area under mixed cereals as would have to be devoted solely to wheat to make our country self-supporting.

B.

The World's Wheat Crop of 1897-98 from Contributory Areas.

	Bushels.
United States	510,000,000
France	240,000,000
Russia and Poland	230,000,000
Austria-Hungary	135,000,000
Germany	105,000,000
Spain	96,000,000
Italy	82,000,000
Trans-Caucasia and Siberia	64,000,000
Argentina	60,000,000
United Kingdom	56,000,000
Canada	55,000,000
Rumania	43,000,000
Caucasia (Northern)	40,000,000
Australasia	38,000,000
Bulgaria	30,000,000
Turkey in Europe	22,000,000
Belgium	16,000,000
Chili	15,000,000
Uruguay, Brazil, &c.	9,000,000
Portugal	7,000,000
Servia	6,000,000
Holland	5,000,000
Denmark	5,000,000
Sweden and Norway	5,000,000
Greece	4,000,000
Switzerland	4,000,000
Bosnia, Montenegro, Cyprus, &c. .	4,000,000
South Africa	4,000,000
	1,890,000,000
Add imports from Asia and North Africa	31,000,000
Total available wheat supply .	1,921,000,000*

Table showing the Variations in the Bread-eating Populations and the Available Supply of Wheat in the Five-Yearly Periods from 1878 to 1897, in Millions of Bushels, and Annual Averages.

Years.	Bread-eating populations.	Wheat grown by "contributory areas."	Imports from Asia and North Africa.	Remainders from former harvest.	Total available supply.	Required for seed and food.	Supply in excess of year's needs.
1877-81	407·0	1797·0	13·8	174·4	1985·2	1812·8	172·4
1882-86	432·8	1937·6	41·4	294·0	2273·0	1946·0	327·0
1887-91	460·8	2043·5	43·2	260·2	2346·9	2102·0	244·9
8192-96	490·9	2199·2	23·6	265·4	2488·2	2233·8	254·4
1897-98	510·0	1890·0	31·0	300·0	2221·0	2310·0	Deficit 89·0

C.

The "world's demand" for wheat is as follows:—

	Bushels.
United Kingdom, about..	180,000,000
Belgium	24,000,000
Germany	35,000,000
Holland	13,000,000
Switzerland	13,500,000
France	40,000,000
Sweden	4,000,000
Spain	10,000,000
Portugal	4,000,000
Greece	4,500,000
Islands and tropical lands	28,000,000
Total	356,000,000

D.

Between 1882 and 1897 the wheat crops were so abundant that over 1200 million bushels were added to our stores, besides large accumulations of rye. During this time of golden harvests, the exports from Russia increased, in consequence of the Russian decline in unit

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* Outside the better known areas of wheat supply a certain proportion of wheat comes from India, Persia, Syria, Anatolia, and North Africa. But it is impossible to get accurate figures as to acreage and yield from these countries; as bread-eaters derive less than 1 per cent of their supplies from these outlying sources, it is convenient to call the ordinary areas "contributory areas," and to deal with the external areas no further than to show the volume of imports yielded from year to year.

consumption of 13·5 per cent. These reserves have been gradually drawn upon, but enough still remained to obscure the fact that the 1895-6 harvest was 75,000,000 bushels, and the 1896-7 harvest was 138,000,000 bushels below current needs.

The following table[*] has been compiled from statistics carefully collected by Mr. Davis and other observers. The prophetic figures are on the assumption that population, unit consumption, and steady development will increase during the next forty-three years as they have increased since 1871:—

Date.	Bread-eaters.	Food and seed[†] required per unit. Bushels.	Requiring bushels of wheat.	With yields averaging 12·7 bushels, acreage required.
1871	371,000,000	4·15	1,540,000,000	121,000,000
1881	416,000,000	4·38	1,822,000,000	143,000,000
1891	472,600,000	4·50	2,127,000,000	167,000,000
1898	516,500,000	4·50	2,324,000,000	183,000,000
1901	536,100,000	4·50	2,412,000,000	190,000,000
1911	603,700,000	4·50	2,717,000,000	214,000,000
1921	674,000,000	4·50	3,033,000,000	239,000,000
1931	746,100,000	4·50	3,357,000,000	264,000,000
1941	819,200,000	4·50	3,686,000,000	290,000,000

To supply these bread-eaters, the world inhabited by bread-eating populations grew the following quantities of wheat in each of the designated five-year periods:—

Years.	Bushels. Annual average.		Acres. Annual average.
1871-75	1,580,000,000,	grown on	131,000,000
1876-80	1,746,000,000	,,	143,000,000
1881-85	1,926,000,000	,,	152,000,000
1886-90	1,987,000,000	,,	154,000,000
1891-95	2,201,000,000	,,	159,000,000

Within the same periods wheat was imported from Asia and North Africa by the "bread-eating" countries as follows:—

Years.	Bushels. Annual average.			Acres. Annual average.
1871-75	8,000,000,	the net	product of	750,000
1876-80	12,000,000	,,	,,	1,120,000
1881-85	36,000,000	,,	,,	3,360,000
1886-90	39,000,000	,,	,,	3,640,000
1891-95	34,000,000	,,	,,	3,200,000

Broadly speaking, 2000 million bushels are now consumed in the countries where they are grown, either as food or for seed, while the balance is exported.

E.

At the present time the disproportion is even higher, owing to unit consumption gradually increasing from year to year accompanied by slow shrinkage in the wheat area.

	1871.	1884.	1897.	Per cent of increase or decrease in twenty-six years.
Population..	371,000,000	432,800,000	510,000,000	37·5 increase.
Wheat acres	125,800,000	154,300,000	158,000,000	25·6 increase.
Rye acres ..	111,000,000	110,300,000	106,500,000	4·1 decrease.

The area planted with the two great bread-making grains is actually less now than thirteen years ago, despite enormous additions to the population. The area under *all* the bread-making grains is absolutely 2·2 per cent less than thirteen years ago, notwithstanding an increase of one-fifth in requirements for bread.

F.

Notwithstanding this expansion the supplies of wheat were hardly sufficient for the food demands of the world. As the area under wheat has increased that under rye has diminished, with the result that scarcely an acre has been added to the world's wheat and rye since 1890; and there was in 1897 a deficit in the two principal bread-making grains of more than 600,000,000 bushels.

G.

Stocks of wheat and flour in the United States were, relatively to population, probably never smaller, if so small as now. The following table (from *Bradstreet*) shows the visible supply of wheat in the States on June 1 since 1893:—

	Bushels.		Bushels.
1893	93,700,000	1896	71,300,000
1894	80,500,000	1897	39,200,000
1895	72,800,000	1898	32,500,000

H.

In 1895 the area under wheat in the Governments of Russia and Poland was 36,000,000 acres. But the yearly consumption of wheat per head during the last ten years has declined 14 per cent, and the consumption of bread is quite 30 per cent less than is required to keep the population in health. The grain reserved for seed has likewise decreased—the peasantry limiting their sowing with the rise of taxation. The reduction of 14 per cent in the unit consumption of bread in Russia has added, during the last eighteen years, 1,360,000,000 bushels to the general wheat supply. This factitious excess temporarily staved off scarcity in Europe.

I.

In the year 1897 there were 2,371,441 acres under cultivation in Manitoba, out of a total of 13,051,375 acres. The total area includes water courses, lakes, forests, towns, and farms, land unsuitable for wheat growing, and land required for other crops.

J.

The most trustworthy estimates give Canada a wheat area of not more than six millions of acres in the next twelve years, increasing to a maximum of twelve millions of acres in twenty-five years. The development of this promising area necessarily must be slow, since prairie land cannot be laid under wheat in advance of a population sufficient to supply the needful labour at seed time and harvest. As population increases so do home demands for wheat.

Acreage, Crop, and Exports of Wheat from Canada from 1891 to 1897.

Year.	Population.	Acres.	Total bushels.	Bushels exported.
1891	4,833,000	2,690,000	62,600,000	3,000,000
1892	4,885,000	2,910,000	49,700,000	10,200,000
1893	4,936,000	2,800,000	42,700,000	11,000,000
1894	4,986,000	2,550,000	44,600,000	11,000,000
1895	5,040,000	2,560,000	57,500,000	9,200,000
1896	5,090,000	2,700,000	40,800,000	10,400,000
1897	5,140,000	2,900,000	56,600,000	8,000,000

The net exports average 8,970,000 bushels yearly, being 24·3 per cent of the net product.

K.

The land under wheat in Austro-Hungary, according to the latest official figures, is eleven million acres. The 1897-8 crop, including that of Croatia-Slavonia, is fifty-five million bushels below that of 1896-7, and as exports

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[*] I have taken the unit consumption including seed at 4·5 bushels and the yield per acre at 12·7 bushels per annum, this being the average of the whole world. The exact yield varies with the country in which wheat is grown, as shown by the following table:—

Average Yield of Wheat per Acre in—

	Bushels.		Bushels.
Denmark	41·8	Poland	16·2
United Kingdom	29·1	Canada	15·5
New Zealand	25·5	Argentina	13·0
Norway	25·1	Italy	12·1
Germany	23·2	United States (mean) .	12·0
Belgium	21·5	India	9·2
Holland	21·5	Russia in Europe ..	8·6
France	19·4	Algeria	7·5
Hungary	18·6	South Australia	7·0
Rumania	18·5	Australasia	6·8
Austria	16·3		

[†] The seed quota is kept constant at 0·6 bushel per unit per annum, but the unit food requirements are found to increase in each five-yearly period. There has been a steady increase of unit wheat requirements by reason of the decrease of unit consumption of rye, maslin, spelt, and buckwheat.

during the last five years have averaged less than 4,000,000 bushels per annum, the imports of wheat are expected to be large.

L.

So long ago as April 16, 1891, the following statement by a leading Indian economist appeared in the *Daily Englishman* of Calcutta:—"People do not realise the fact that all the wheat India produces is required for home consumption, and that this fact is not likely to be realised until a serious disaster occurs, and that even now less than 9 per cent is exported. It is a self-evident fact that a slight expansion of consumption, or a partial failure of crops of other food grains, will be sufficient to absorb the small proportion now exported. Besides, we have a steady increase of consumption, in consequence of the natural growth of the population, as well as in the gradual improvement of the condition of a considerable part of the people in the cities. I believe that, comparatively speaking, India will in a few years cease to export wheat, and soon thereafter become an importing country."

M.

An average wheat crop on the 1897-8 acreage would be 2,070,000,000 bushels. Adding to this 1,270,000,000 bushels, makes a grand total of 3,340,000,000 bushels. But the estimate in Appendix D shows that in the year 1931 the bread eaters will require 3,357,000,000 bushels. Thus there will be in 1931 a deficiency of 17,000,000 bushels, unless the average yield per acre be increased.

N.

Sir Andrew Noble informs me that a first-class battleship would carry about sixty-three tons of cordite, and we may suppose that in a general action forty tons of this would be expended. Now at Trafalgar, Nelson had twenty-seven line-of-battle ships, and the allied forces thirty-three. If we suppose a similar number of modern battleships and first-class cruisers to be engaged, and each to expend forty tons of cordite, the total volume of nitrogen set free would be 302,400 cubic metres, or about 380 tons, equivalent to 2300 tons of nitrate of soda.

ADDRESS TO THE CHEMICAL SECTION
OF THE
BRITISH ASSOCIATION.

Bristol, 1898.

By Professor F. R. JAPP, M.A., LL.D., F.R.S.,
President of the Section.

Stereochemistry and Vitalism.

Of the numerous weighty discoveries which science owes to the genius of Pasteur, none appeals more strongly to chemists than that with which he opened his career as an investigator—the establishing of the connection between optical activity and molecular symmetry in organic compounds. The extraordinary subtlety of the modes of isomerism then for the first time disclosed; the novelty and refinement of the means employed in the separation of the isomerides; the felicitous geometrical hypothesis adopted to account for the facts—an hypothesis which subsequent investigation has served but to confirm; the perfect balance of inductive and deductive method; and lastly, the circumstance that in these researches Pasteur laid the foundation of the science of stereochemistry: these are characteristics any one of which would have sufficed to render the work eminently noteworthy, but which, taken together, stamp it as the capital achievement of organic chemistry.

Physiologists, on the other hand, are naturally more attracted by Pasteur's subsequent work, in which the biological element predominates; in fact, I doubt whether many of them have given much attention to the earlier work. And yet it ought to be of interest to physiologists, not merely because it is the root from which the later work springs, but because it furnishes, I am convinced, a reply to the most fundamental question that physiology can propose to itself—namely, whether the phenomena of life are wholly explicable in terms of chemistry and physics; in other words, whether they are reducible to problems of the kinetics of atoms, or whether, on the contrary, there are certain residual phenomena, inexplicable by such means, pointing to the existence of a directive force which enters upon the scene with life itself, and which, whilst in no way violating the laws of the kinetics of atoms—whilst, indeed, acting through these laws—determines the course of their operation within the living organism.

The latter view is known as Vitalism. At one time universally held, although in a cruder form than that just stated, it fell, later on, into disrepute; "vital force," the hypothetical and undefined cause of the special phenomena of life, was relegated to the category of occult qualities; and the problems of physiology were declared to be solely problems of chemistry and physics. Various causes contributed to this result. In the first place, the mere name "vital force" explains nothing; although, of course, one may make this admission without thereby conceding that chemistry and physics explain everything. Secondly, the older vitalists confounded force with energy; their "vital force" was a source of energy; so that their doctrines contradicted the law of the conservation of energy, and became untenable the moment that this law was established. I would point out, however, that the assumption of a purely directive "vital force," such as I have just referred to, using the word "force" in the sense which it bears in modern dynamics, does not *necessarily* involve this contradiction; for a force acting on a moving body at right angles to its path does no work, although it may continuously alter the direction in which the body moves. When, therefore, Professor J. Burdon Sanderson writes—"The proof of the non-existence of a special 'vital force' lies in the demonstration of the adequacy of the known sources of energy in the organism to account for the actual day by day expenditure of heat and work," he does not consider this special case. The application of the foregoing principle of dynamics to the discussion of problems like the present is, I believe, due to the late Professor Fleeming Jenkin. A third ground for abandoning the doctrine of a "vital force" was the discovery that numerous organic compounds for the production of which the living organism was supposed to be necessary, could be synthesised by laboratory methods from inorganic materials. It is the validity of some of the conclusions drawn from the latter fact that I wish especially to consider.

Recent years, have, however, witnessed a significant revival of the doctrine of vitalism among the physiologists of the younger generation.

It is not my intention to offer any opinion on the various arguments which physiologists of the neo-vitalistic school have put forward in support of their views; these arguments and the facts on which they are based lie entirely outside my province. I shall confine myself to a single class of chemical facts rendered accessible by Pasteur's researches on optically active compounds, and, considering these facts in the light of our present views regarding the constitution of organic compounds, I shall endeavour to show that living matter is constantly performing a certain geometrical feat which dead matter, unless indeed it happens to belong to a particular class of products of the living organism and to be thus ultimately referable to living matter, is incapable—not even conceivably capable—of performing. My argument, being based on geometrical and dynamical considerations, will have the advantage, over the physiological arguments, of immeasurably greater simplicity; so that, at all events, any fallacy into which I may unwittingly fall will be the more readily detected.

In order to make clear the bearing of the results of stereochemical research on this physiological problem, it will be necessary to give a brief sketch of the stereochemistry of optically active organic compounds, as founded by Pasteur and as further developed by later investigators.

Substances are said to be optically active when they produce rotation of the plane of polarisation of a ray of polarised light which passes through them. The rotation may be either to the right or to the left, according to the nature of the substance; in the former case the substance is said to be dextro-rotatory; in the latter, lævo-rotatory. The effect is as if the ray had been forced through a twisted medium—a medium with a right-handed or a left-handed twist—and had itself received a twist in the process; and the amount of the rotation will depend upon the degree of "twist" in the medium (that is, on the rotatory power of substance) and upon the thickness of the stratum of substance through which the ray passes, just as the angle through which a bullet turns in passing from the breech to the muzzle of a rifle will depend upon the degree of twist in the rifling and the length of the barrel. If the bullet had passed through the barrel in the opposite direction, the rotation would still have been in the same sense; since a right-handed (or left-handed) twist or helix remains the same from whichever end it is viewed, in whichever direction it is traversed. This also applies to optically active substances; if the polarised ray passes through the substance in the opposite direction, the rotation still occurs in the same sense as before. This characteristic sharply distinguishes the rotation due to optically active substances from that produced by the magnetic field, the latter rotation being reversed on reversing the direction of the polarised ray.

Optically active substances may be divided into two classes. Some, like quartz, sodium chlorate, and benzil, produce rotation only when in the crystallised state; the dissolved (or fused) substances are inactive. Others, like oil of turpentine, camphor, and sugar, are optically active when in the liquid state or in solution. In the former case the molecules of the substance have no twisted structure, but they unite to form crystals having such a structure. As Pasteur expressed it, we may build up a spiral staircase—an asymmetric figure—from symmetric bricks; when the staircase is again resolved into its component bricks, the asymmetry disappears. (I will explain presently the precise significance of the terms symmetry and asymmetry as used in this connection). In the case of compounds which are optically active in the liquid state, the twisted structure must be predicated of the molecules themselves; that is, there must be a twisted arrangement of the atoms which form these molecules.

The earliest known experimental facts regarding the rotation of the plane of polarisation by various substances, solid and liquid, were discovered by Arago and by Biot.

After this preliminary statement as to what is understood by optical activity, we may consider Pasteur's special contributions to the solution of the problems involved.

Pasteur tells us, in the well-known "Lectures on the Molecular Asymmetry of Natural Organic Products," which he delivered in 1860, before the Chemical Society of Paris, that his earliest independent scientific work dealt with the subject of crystallography, to which he had turned his attention from a conviction that it would prove useful to him in the study of chemistry. In order to perfect himself in crystallographical methods, he resolved to repeat all the measurements contained in a memoir by De la Provostaye on the crystalline forms of tartaric acid, racemic acid, and their salts. These two sets of compounds have the same composition, except that they frequently differ in the number of molecules of water of crystallisation which they contain; but whereas tartaric acid and the tartrates are dextro-rotatory, racemic acid and the racemates are optically inactive. It was probably this circumstance that decided Pasteur in his choice of a subject, for it appears that, even as a student, he had been attracted by the problem of optical activity. In the course of the repetition, however, he detected a fact which had escaped the notice of his predecessor in the work, accurate observer as the latter was—namely, the presence, in the tartrates, of right-handed hemihedral faces, which are absent in the racemates. Hemihedral faces are such as occur in only half their possible number; and in the case of non-superposable hemihedry, to which class that of the tartrates belongs, there are always two opposite hemihedral forms possible—a right-handed or dexto- form, and a left handed or lævo- form. Which is right, and which is left, is a matter of convention; but they are opposite forms, and differ from one another exactly as the right hand of the human body differs from the left: that is, they resemble one another in every respect, except that they are non-superposable—the one cannot be made to coincide in space with the other, just as a right hand will not fit into a left-hand glove. The one form is identical with the mirror image of the other: thus the mirror image of a right hand is a left hand. Such opposite hemihedral crystalline forms are termed *enantiomorphs*; they have the same faces and the same angles, but differ in the fact that all positions in the one are reversed in the other for one dimension of space, and left unchanged for the other two dimensions; this being the geometrical transformation which an object appears to undergo when reflected in a plane mirror. Enantiomorphism is possible only in the case of asymmetric solid figures: these alone give non-superposable mirror images. Any object which gives a mirror image identical with the object itself—a superposable mirror image—must have at least one plane of symmetry.

The hemihedry of the tartrates discovered by Pasteur is in every case in the same sense—that termed right-handed—provided that the crystals are oriented according to two of the axes which have nearly the same ratio in all the tartrates.

Pasteur was inclined to connect the molecular dextro-rotatory power of the tartrates with this right-handed hemihedry; since in the racemates both the hemihedry and the rotatory power were absent. A similar connection, which, however, held good only for the crystalline condition, had, as he points out, been already observed in the case of quartz, the crystals of which occasionally exhibit small asymmetric (tetartohedral) faces, situated in some specimens to the right and in others to the left; the former specimens being dextro-, the latter lævo-rotatory. The possibility of this connection was first suggested by Sir John Herschel.

Pasteur's views were confirmed by an unexpected discovery which he made shortly after. Mitscherlich had stated, in 1844, in a communication to Biot, which the latter laid before the French Academy of Sciences, that sodium ammonium tartrate and sodium ammonium racemate were identical, not merely in chemical composition, but in crystalline form, in specific gravity, and in every other property, chemical and physical, except that the solution of the former salt was dextro-rotatory, that of the latter inactive. And to make his statement still more definite, he added:—"The nature and the number of the atoms, their arrangement, and their distances from one another, are the same in both compounds."

At the time this passage appeared, Pasteur was a student in the Ecole Normale. He tells us how it puzzled him, as being in contradiction to the views universally held by physicists and chemists that the properties, chemical and physical, of substances depended on the nature, number, and arrangement of their constituent atoms. He now returned to the subject, imagining that the explanation would be found in the fact that Mitscherlich had overlooked the hemihedral faces in the tartrate, and that the racemate would not be hemihedral. He therefore prepared and examined the two double salts. He found that the tartrate was, like all the other tartrates which he had investigated, hemihedral; but, to his surprise, the solution of the racemate also deposited hemihedral crystals. A closer examination, however, disclosed the fact that, whereas in the tartrate all the hemihedral faces were situated to the right, in the crystals from the solution of the racemate they were situated sometimes to the right and sometimes to the left. Mindful of his view, regarding the connection between the sense of the hemihedry and that of the optical activity, he carefuly picked out and separated the dextro- and lævo-hemihedral crystals, made a solution of each kind separately, and observed it in the polarimeter. To his surprise and delight, the solution of the right-handed crystals was dextro-rotatory; that of the left-handed, lævo-rotatory. The right-handed crystals were identical with those of the ordinary (dextro-) tartrate; the others, which were their mirror image, or enantiomorph, were derived from the hitherto unknown lævo-tartaric acid. From the dextro- and lævo-salts, thus separated, he prepared the free dextro- and lævo-tartaric acids. And having thus obtained from racemic acid its two component acids—dextro- and lævo-tartaric acids—it was an easy matter to re-compose racemic acid. He found that, on mixing equal weights of the two opposite acids, each previously dissolved in a little water, the solution almost solidified, depositing a mass of crystals of racemic acid.

These two tartaric acids have the same properties, chemical and physical, except where their opposite asymmetry comes into play. They crystallise in the same forms, with the same faces and angles; but the hemihedral facets, which in the one are situated to the right, are, in the other, situated to the left. Their specific gravities and solubilities are the same; but the solution of the one is dextro-rotatory; of the other, lævo-rotatory. The salts which they form with inorganic bases also agree in every respect, except as regards their opposite asymmetry and opposite rotatory power. They are enantiomorphous.

Pasteur, discussing the question of the molecular constitution of these acids, anticipates in a remarkable manner the views at present held by chemists. "We know, on the one hand," he says, "that the molecular structures of the two tartaric acids are asymmetric, and on the other, that they are rigorously the same, with the sole difference of showing asymmetry in opposite senses. Are the atoms of the right acid grouped on the spirals of a right-handed helix, or placed at the solid angles of an irregular tetrahedron, or disposed according to some particular asymmetric grouping or other? We cannot answer these questions. But it cannot be a subject of doubt that there exists an arrangement of the atoms in an asymmetric order having a non-superposable image. It is not less certain that the atoms of the left acid realise precisely the asymmetric grouping which is the inverse of this."

The idea of the irregular tetrahedron is, it may be explained, derived from the hemihedral facets. Imagine these to develop in the case of dextro-tartaric acid until the other faces of the crystal disappear, and there results an irregular tetrahedron. Repeat the process with a crystal of lævo-tartaric acid, and the enantiomorphous tetrahedron—the mirror-image of the former—is obtained. We shall see later that the idea, on the one hand, of two asymmetric tetrahedra, and, on the other, that of two opposite helices, given as alternatives by Pasteur to explain the grouping of the atoms within the molecules of dextro- and lævo-tartaric acids, are in reality identical.

The precision of Pasteur's views as to the asymmetry of these acids enabled him to discover two further methods of separating them. Thus he points out that although these acids will possess equal affinity for any given symmetric base, such as potash, or ammonia, or aniline, yet their affinities will not be equal if the base, like quinine or strychnine, is itself asymmetric; because here the special one-sided asymmetry of the base will modify its mode of combination with the two enantiomorphous acids. The solubility is different in the case of the dextro- and lævo-tartrates of the same asymmetric base; the crystalline form, the specific gravity, the number of molecules of water of crystallisation, may be all different. Potassium dextro- and lævo-tartrates are mirror-images of one another; quinine dextro- and lævo-tartrates are not. Pasteur employed in his experiments the asymmetric base cinchonicine, which he converted into its acid racemate, and allowed the solution to crystallise. The first crystallisations consisted of pure lævo-tartrate of cinchonicine, whilst the more soluble dextro-tartrate remained in the mother-liquor, from which it finally crystallised in forms totally distinct from those of the lævo-tartrate.

Pasteur's third method is of physiological interest, and is, moreover, the stepping-stone to his later work on ferments. As we shall see presently, he regarded the formation of asymmetric organic compounds as the special prerogative of the living organism. Most of the substances of which the animal and vegetable tissues are built up—the proteids, cellulose—are asymmetric organic compounds, displaying optical activity. Pasteur had shown that two compounds of inverse asymmetry behaved differently towards a third asymmetric compound How would they behave towards the asymmetric living organism?

It had frequently been noticed that impure calcium tartrate, when mixed with organic matters, as is the case when it is obtained in the process of preparing tartaric acid from argol, readily underwent fermentation. Pasteur examined the action of the ferment (apparently a *Penicillium*) on ammonium tartrate—a substance which had the advantage over calcium tartrate of being soluble —and finding that the fermentation here followed a normal course, ending with the destruction of the tartrate, repeated the experiment with ammonium racemate, examining the solution from time to time with the polarimeter. The fermentation proceeded, apparently, as before; but the solution, originally optically inactive, became lævo-rotatory, the activity gradually increasing in amount until a maximum was reached. At this point the fermentation ceased. The whole of the dextro-tartrate had disappeared, and from the solution the lævo-tartrate was obtained in a state of purity. The asymmetric living organism had selected for its nutriment that particular asymmetric form of tartaric acid which suited its needs—the form, doubtless, which in some way fitted its own asymmetry—and had left the opposite form either wholly or, for the most part, untouched. The asymmetric microorganism, therefore, exhibits a power which no symmetric chemical substance, such as our ordinary oxidising agents, and no symmetric form of energy, such as heat, can ever possess: it distinguishes between enantiomorphs. If we oxidise racemic acid with nitric acid, for example, both the enantiomorphous constituents are attacked in exactly the same degree. If we heat racemic acid, whatever happens to its right-handed constituent happens equally to its left-handed constituent: the temperature of decomposition of both is the same. Asymmetric agents can alone display selective action in dealing with enantiomorphs.

By the action of heat Pasteur converted ordinary tartaric acid into racemic acid, in which process a portion of the right acid is converted into the left, an equilibrium being established; and lævo-tartaric acid may be converted into racemic acid in the same way, the inverse change taking place. At the same time, a new tartaric acid is formed in both cases: mesotartaric acid, or true inactive tartaric acid, which resembles racemic acid in having no action on the plane of polarisation, but differs from it in not being separable into two acids of opposite activity. According to our present views, it contains two equal and opposite asymmetric groups *within* its molecule. Racemic acid is thus inactive by *inter*molecular compensation; mesotartaric acid by *intra*molecular compensation.

Pasteur, generalising somewhat hastily from the few cases which he had studied, came to the conclusion that all organic compounds capable of exhibiting optical activity might exist in the foregoing four forms—dextro, lævo, racemoid, and meso. As regards the dextro and lævo forms, this is correct; as regards the racemoid form it is generally correct; but the meso form, as we now know, is a very special case, implying that the molecule contains two structurally identical complexes of opposite asymmetry.

Were I following the exact historical order, I should introduce here Pasteur's view that compounds exhibiting optical activity have never been obtained without the intervention of life—a view which it is the object of the present address to consider. The later developments of stereochemistry, however, throw so much light on this question, and enable us to discuss it with such precision, that we shall turn our attention to these first. Before so doing, however, we may note that, in spite of the immense growth in the material of stereochemistry, and in spite of the development of the theoretical views of stereochemists, hardly any experimental method of fundamental importance for the separation and transformation of optically active compounds has been added to those described in Pasteur's classical researches, although it is almost forty years since these came to a close. Perhaps Walden's remarkable discovery of a method for the transformation of certain enantiomorphs into their optical opposites without previous racemisation, is the only one entitled to be so classed.

Pasteur was in advance of his time, and his theory of molecular asymmetry was a seed that lay for many years in the ground without germinating.

In 1858, just about the period when Pasteur was concluding his researches in the foregoing field, Kekulé published his celebrated theoretical paper, "On the Constitution and Metamorphoses of Chemical Compounds, and on the Chemical Nature of Carbon," in which he showed that, by assuming that the carbon atom had four units of affinity, the constitution of organic compounds could be satisfactorily explained. This was the starting-point of the theory of chemical structure, and from that time to the present day organic chemists have been engaged, with enormous expenditure of labour, in determining the constitution or molecular structure of the carbon compounds on the lines of Kekulé's theory.

In order that Pasteur's ideas should bear fruit it was only necessary that his purely general statements with regard to molecular asymmetry should be specialised, so as to include the recognised constitution of organic compounds. It was from this union of Pasteur's theory with that of Kekulé that modern stereochemistry sprang. The necessary step was taken, independently and almost simultaneously, by van 't Hoff and Le Bel, in 1874. I will briefly state their conclusions, so far as these bear on the subject of optical activity.

If we examine the structural formulæ of a number of thoroughly investigated optically active organic compounds, we shall find that the molecule of each contains at least one carbon atom of which the four affinities are satisfied by four different atoms or groups—an asymmetric carbon atom, as it is termed.

The four affinities, or directed attractive powers, of the carbon atom are not to be conceived of as lying in one plane. The simplest assumption that we can make with regard to their distribution in space is that the direction of each makes equal angles with the directions of the three others. We may express this differently by saying that the four atoms or groups attached to the carbon atom are situated at the solid angles of a tetrahedron, in the centre of which the carbon atom itself is placed. If the four atoms or groups are all identical they will be equally attracted by the carbon atom; consequently they will be equidistant from it, and the tetrahedron will be regular. If they are all different the force with which each is attracted will be different; they will arrange themselves at different distances from the carbon atom; and the tetrahedron will be irregular: it will have no plane of symmetry. Any compound of the formula $CHX'Y'Z'$ can therefore exist in two enantiomorphs, applying this term to the molecules themselves—in two non-superposable forms, each of which is the mirror image of the other: thus—

Fig. 1.

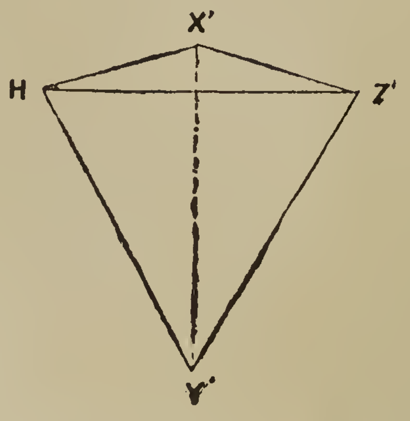
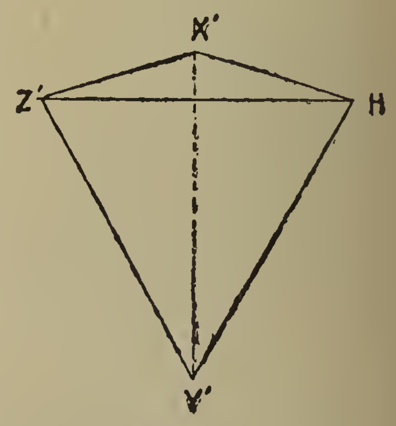


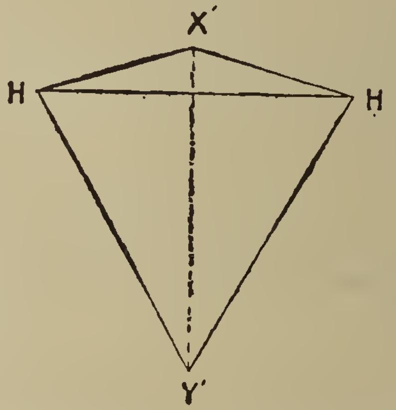
Fig. 2.



(In these figures no attempt has been made to represent the tetrahedra as irregular; the opposite asymmetry is indicated merely by the opposite order of the four attached atoms or groups. In reality, however, they would be irregular. The carbon atom itself is not shown).

If we consider any particular set of three atoms or groups—for example, H, Z', and Y'—looking towards that face of the tetrahedron about which they are arranged, any order, thus HZ'Y', which is clockwise in one figure, will be counter-clockwise in the other. In like manner, a continuous curve, passing through the four atoms or groups in any given sequence, will form a right-handed helix in the one case and a left-handed helix in the other. We thus find that the foregoing assumptions—the very simplest that could be made—regarding the distribution of the four affinities of carbon and the different degree with which four different atoms or groups will be attracted by the carbon atom to which they are attached, lead to the asymmetric structures postulated by Pasteur to account for optical activity—namely, enantiomorphous irregular tetrahedra, and right- and left-handed helices.

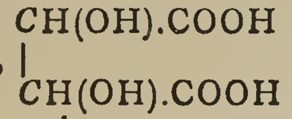
Fig. 3.



That a spiral arrangement, right- or left-handed, will produce rotation of the plane of polarisation in its own sense, may be shown by various experiments: thus in Reusch's optically active piles of plates of mica, produced by crossing successive plates of biaxal mica at an angle of 60° to one another; or in the twisted jute fibres recently described by Professor Bose, which, according to the direction of the twist previously imparted to them, rotate the plane of polarisation of electric waves either to the right or to the left.

If two of the four atoms or groups attached to carbon are identical, there is no asymmetry, and no optical activity. Thus, in a compound of the formula $CH_2X'Y'$, which we may represent by our tetrahedral scheme as shown in fig. 3, the two hydrogen atoms are equidistant from the carbon atom; the system has a plane of symmetry passing through X' Y' and the carbon atom, and has therefore a superposable mirror image.

If the molecule contains only one asymmetric carbon atom, the latter may be either positive or negative, so that the substance may exist in two forms of opposite optical activity; in addition to which we may have the racemoid combination of the two, which will be inactive but separable. Mandelic acid, $C_6H_5.\mathit{C}H(OH).COOH$,* is a case in point: it is known in these three forms.

If, as in the case of tartaric acid,  $\begin{array}{l}\mathit{C}H(OH).COOH\\ |\\ \mathit{C}H(OH).COOH\end{array}$, the molecule contains two asymmetric carbon atoms, and at the same time consists of two structurally identical halves, then these two atoms may be either both positive or both negative, reinforcing each other's effect in either case; or one may be positive and the other negative, when, owing to the structural identity of the two halves of the molecule, the effect of the one will exactly compensate that of the other, and the compound will be inactive, but not separable. Furthermore, there may be the racemic combination of the bi-dextro form with the bi-lævo form—a combination inactive, but separable. We have thus the explanation of the four forms observed by Pasteur.

In fact all the complex cases of isomerism that have been met with among compounds of this class—compounds structurally identical, but configuratively distinct, as it is termed—may be satisfactorily explained, and their possible number accurately predicted, by means of the theory of the asymmetric carbon atom.

I must apologise to the organic chemists among my audience for inflicting on them this very elementary exposition of what to them is a well-known theory. But outside the circle of organic chemists the theory is, I fear, far from well known. Thus, an eminent physicist, in his "Theory of Light," referring to the rotation of the plane of polarisation by liquid or dissolved substances, says:—"I am not aware that any explanation of it has ever been suggested." And in the *Proceedings of the Royal Society* for the present year, another eminent physicist, after quoting with approval this purely personal confession, goes on to suggest the possibility of the molecules having a twisted structure, and points out that a right-handed twist "would appear right-handed when looked at from either end," apparently unaware that such conceptions have been commonplaces of stereochemistry for the past quarter of a century at least.

This brief sketch of the theory was therefore necessary in order that we may now effectively discuss Pasteur's views on the relation between optical activity and life.

Whenever we prepare artificially, starting either with the elements or with symmetric compounds, any organic compound which, when it occurs as a natural product of the living organism, is optically active, the primary product of our laboratory reactions, however closely it may in other respects resemble the natural product, differs from it in being optically inactive. Pasteur was greatly impressed by this fact. In the Lectures delivered in 1860 he says:—"Artificial products have no molecular asymmetry; and I could not point out the existence of any more profound distinction between the products formed under the influence of life, and all others." And again, he refers to "the molecular asymmetry of natural organic products," as "the great characteristic which establishes perhaps the only well-marked line of demarcation that can at present be drawn between the chemistry of dead matter and the chemistry of living matter." He would not admit that even racemoid forms, optically inactive by intermolecular compensation, might be artificially prepared; thus, to the suggestion that the malic acid which he had obtained from Dessaignes's artificial aspartic acid might possibly be the racemoid form (as we now know that it is), he replied:—"That is improbable, for then not only should we have made an active body from an inactive one, but we should have made two—a right and a left."

The view that racemoids could not be prepared artificially did not long remain tenable. In 1860, the year in which the foregoing lectures were delivered, Perkin and Duppa, and, independently, Kekulé, obtained from dibromsuccinic acid a form of tartaric acid, which Pasteur recognised as racemic acid. But the succinic acid employed had been prepared from amber, a substance of vegetable origin; and there was still the possibility that herein lay the source of the optical activity of the two constituents of the artificial racemic acid. This objection, which was raised by Pasteur himself, fell to the ground when, in 1873, Jungfleisch prepared racemic acid from Maxwell Simpson's synthetic succinic acid, and separated it into its right and left constituents by means of the sodium ammonium salt.

"Thus falls the barrier," wrote Schützenberger, "which M. Pasteur had placed between natural and artificial products. This example shows us how reserved we must be in attempting to draw distinctions between the chemical reactions of the living organism and those of the laboratory."

To these words, which, although written a quarter of a century ago, may fairly be taken as representing the prevailing belief of chemists at the present day, Pasteur replied as follows:

"Contrary to M. Schützenberger's belief this barrier still exists. . . . To transform *one inactive compound into another inactive compound* which has the power of resolving itself simultaneously into a right-handed compound and its opposite (*son symétrique*), is in no way comparable with the possibility of transforming *an inactive compound into a single active compound*. This is what no one has ever done; it is, on the other hand, what living nature is doing unceasingly before our eyes."

On this and subsequent occasions Pasteur did little more than reiterate opinions which he had previously expressed. As he himself stated, he was then occupied with other problems which absorbed his entire time and energies. The result has been that the opinions have suffered neglect and even misrepresentation. Thus Ostwald, in his *Allgemeine Chemie*, translating, or rather paraphrasing, the foregoing passage, omits the word "single"—which is the key to Pasteur's meaning—and then condemns the statement as illogical.

Pasteur's point is, that whereas living nature can make a *single* optically active compound, those laboratory reactions, to which we resort in synthesising such compounds, always produce, simultaneously, at least *two* of equal and opposite optical activity, the result being intermolecular compensation and consequent optical inactivity. Not necessarily implied in Pasteur's statement, but entirely in harmony with it, is the fact that we can sometimes produce artifically a single compound containing, within its molecule, two equal and opposite asymmetric groups, and therefore inactive by *intra*molecular compensation; thus in the oxidation of maleic acid to mesotartaric acid.

Let us consider the cause of this limitation of our synthetic reactions. Why cannot we produce, by laboratory processes, involving the play of symmetric forces and the interaction of symmetric atoms and molecules, *single* optically active compounds? To answer that question let us turn our attention to the mechanism of the change in which a symmetric carbon atom becomes asymmetric.

A simple case of such a change, typical of all similar changes, is the transformation of a compound, $CH_2X'Y'$, by substitution, into $\mathit{C}HX'Y'Z'$. If we follow this process by means of our tetrahedral model we see at once why, in our ordinary laboratory reactions, both enantiomorphs must be generated in equal quantity. The molecule of the compound, $CH_2X'Y'$, of which the tetrahedral representation is given in fig. 3, has, as we have already seen, a plane of symmetry passing through $X'Y'$ and the carbon atom; and from this plane of symmetry the two hydrogen atoms are equidistant on opposite sides. Any purely mechanical, symmetric force, therefore—any force, for example, such as comes into play in the motions of the symmetric molecules of a gas or a liquid—which affects one of these hydrogen atoms in one molecule of the com-

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* The asymmetric carbon atom is represented by an italic *C*.

pound $CH_2X'Y'$, has an equal chance of affecting the other hydrogen atom in another molecule. If the right-hand hydrogen atom in fig. 3 is replaced by the radicle Z′, we obtain the enantiomorph represented in fig. 1; if the left-hand hydrogen atom, that represented in fig. 2. The chances in favour of these two events being equal, the ratio,

$$\frac{\text{Number of occurrences of event I.}}{\text{Number of occurrences of event II.}}$$

will, if we are dealing with an infinitely great number of molecules, approximate to unity. We therefore obtain a mixture, optically inactive by intermolecular compensation.

All cases of the conversion of symmetric into asymmetric compounds may be referred to the same category, no matter whether the chemical process is one of substitution or of addition, or whether the resulting molecule contains one or more asymmetric carbon atoms. Thus, in the reduction of a ketone of the formula $X'.CO.Y'$ to a secondary alcohol of the formula $X'.CH(OH).Y'$; in the transformation of an aldehyde by the addition of hydrocyanic acid into a nitrile of an α-hydroxy-acid; in the oxidation of fumaric acid to racemic acid—cases typifying the various additive processes in which asymmetric groupings are produced—there is one condition common to all: in the symmetric compound, with which we start, there are, in every case, two identical points of attack, equidistant from the plane of symmetry of the molecule, and the result is that the two possible events happen in equal number, so that the mixture of enantiomorphs obtained is optically inactive by compensation. We are, of course, in many cases able afterwards to separate these enantiomorphs by the methods devised by Pasteur, and thus obtain the single optically active compounds; but we cannot produce them singly as long as we have at our disposal only the symmetric forces which we command in the laboratory.

Precisely the same state of things prevails when symmetric molecules unite, under the influence of symmetric forces, to build up an asymmetric crystalline structure. When, for example, sodium chlorate crystallises from its aqueous solution, the number of right-handed crystals is, on the average, as was shown by Kipping and Pope, equal to the number of left-handed crystals. The same fact was proved by Landolt by observing the optical inactivity of the mixture of microscopic right and left crystals obtained by adding alcohol to a concentrated aqueous solution of sodium chlorate. The two possible asymmetric events occur in equal number.

Non-living, symmetric forces, therefore, acting on symmetric atoms or molecules, cannot produce asymmetry, since the simultaneous production of two opposite asymmetric halves is equivalent to the production of a symmetric whole, whether the two asymmetric halves be actually united in the same molecule, as in the case of mesotartaric acid, or whether they exist as separate molecules, as in the left and right constituents of racemic acid. In every case the symmetry of the whole is proved by its optical inactivity.

The result is entirely different, however, when we allow symmetric forces to act under the influence of already existing asymmetric, non-racemoid compounds.

Thus if we start with an optically active compound—a compound containing one or more asymmetric carbon atoms and non-racemoid—and, by appropriate chemical reactions, render asymmetric some carbon atom in the compound which was not previously so, then it does not follow that the two forms represented by the two possible arrangements of this new asymmetric carbon atom will be produced in equal quantity. The compound with which we start has no plane of symmetry; and, although there are still the two possible points of attack, one will be more exposed than the other; in fact, one mode of attack may so predominate that apparently only one asymmetric compound is formed, the other compound, if formed at all, escaping detection by the smallness of its amount. A case in point is the conversion of *d*-mannose by combination with hydrocyanic acid into the nitrile of *d*-mannoheptonic acid, studied by Emil Fischer, in which only one nitrile is formed, although there are two ways in which the hydrocyanic acid may attach itself to the aldehyde group of the mannose. On the other hand, the same general reaction, in the union of hydrocyanic acid with ordinary aldehyde $CH_3.CHO$—a symmetric compound—yields the right and left forms of lacto-nitrile $CH_3.CH(OH).CN$ in equal quantity, the two asymmetric events occurring in equal number, and the resulting mixture of compounds being inactive. It is the difference between guidance and no guidance: the asymmetric group present in the mannose guides into a particular path the symmetric forces which bring about the addition of the hydrocyanic acid; in the case of the symmetric aldehyde the result is left to pure chance. The latter action is like that of tossing a perfectly balanced coin; in the former the coin is heavily weighted on one side. The saying, "*les dés de la Nature sont pipés*," is certainly true of living nature and its products.

This guiding action displayed by asymmetric compounds may even impart a bias to the crystallisation of those molecularly symmetric substances already referred to, which crystallise in enantiomorphous forms. Thus Kipping and Pope have recently made the interesting observation that the crystals of sodium chlorate which are deposited from an aqueous solution containing 200 grms. of *d*-glucose to the litre consist, on an average, of about 32 per cent of right-handed to 68 per cent of left-handed crystals, the asymmetric carbohydrate, by its mere presence, favouring the formation of the one asymmetric form of the inorganic salt at the expense of the other.

(To be continued).

HYDROMETERS OF TOTAL IMMERSION.*

By A. W. WARRINGTON, M.Sc.

The writer has made a series of experiments with the object of showing that the hydrometer becomes an instrument of scientific precision if it is modified so that when used it is totally immersed in the liquid.

Small ring-shaped platinum weights are slipped over the ungraduated neck of a glass hydrometer until the latter has nearly attained the specific gravity of the liquid to be tested. The temperature of the liquid is then slowly altered until the hydrometer and the liquid have exactly the same specific gravity.

With proper precautions this method gives results accurate to one in a million for temperatures from 0° to 40° C.

To determine the specific gravity of a solid use is made of a glass hydrometer of total immersion, which in form is not unlike a Nicholson hydrometer which has lost its tray. Two experiments are made at approximately the same temperature; in one of which the hydrometer is weighted only with pure mercury, and in the other it is weighted with the solid together with the necessary amount of mercury. As in the determination of the specific gravity of a liquid, the temperature is determined at which the hydrometer has no weight in water. The results are accurate to one in a hundred thousand.

An Honour.—Dr. A. B. Griffiths has been elected an Honorary Member of the Medical and Surgical Society of Rio Janeiro, Brazil, in recognition of his researches on the ptomaines.

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* Abstract of a Paper read before the British Association (Section A), Bristol Meeting, 1898.

SOME PRINCIPLES AND METHODS OF ANALYSIS APPLIED TO SILICATE ROCKS.*

By W. F. HILLEBRAND.

(Continued from p. 107).

Alkalis.

The Lawrence Smith Method.— With the exception of a few determinations made in the early days of the Survey's existence, all alkali determinations have been made by the method of J. Lawrence Smith (*Am. Journ. Sci.*, 2nd series, vol. l., p. 269, 1871; *Am. Chemist*, vol. i., 1871; *Annalen Chem. und Pharm.*, vol. clix., p. 82, 1871), which is far more convenient than, and fully as accurate as, the older one, in which decomposition is effected by hydrofluoric and sulphuric acids. One of its chief advantages is the entire elimination of magnesia at the start.

The ammonium chloride used must be purified, preferably by sublimation, or by neutralising pure ammonia by pure hydrochloric acid, and the calcium carbonate is best obtained from pure calcite by solution and re-precipitation. However obtained, this last is not entirely free from alkalis, which must be estimated once for all in order to apply a correction. Eight grms. of the carbonate will contain usually from 0·0012 to 0·0016 grm. of alkaline chlorides, almost entirely the sodium salt, but the amount has been brought down to half the above by very long washing. This correction may be admitted at once to be a defect of the method, but it is one easily applied with safety.

The ignition may be made in a covered crucible of ordinary shape and of about 20 to 30 c.c. capacity, but the heat has to be kept so low in this case to avoid loss by volatilsation that perfect decomposition is not always assured. Hence, to avoid waste of time in very fine grinding, the form of crucible with cap, originally advocated by Smith, is very much to be preferred, since it permits, when set at an angle through an opening in the side of a fire-clay cylinder, of the application of the full heat of two burners, and perfect decomposition invariably results without the need of extraordinary care in grinding. The crucible used in this laboratory for ½ grm. of rock powder and 4 grms. calcium carbonate is 8 c.m. long, 1·8 c.m. wide at the mouth, and 1·5 at the bottom. For double the amounts or more the dimensions are 8 c.m., 2·5 c.m., and 2·2 c.m. The weights are 25 and 40 grms.

Perfectly satisfactory results are to be obtained with but a ½ grm. of rock powder. This is weighed out, ground down somewhat finer in a large agate mortar, mixed with its own weight of sublimed ammonium chloride, and the two thoroughly ground together. Then nearly all of 4 grms. of calcium carbonate is added, and the grinding continued till a thorough mixing has resulted. The contents of the mortar are transferred to the long crucible, the rest of the carbonate being used for rinsing off mortar and pestle. The crucible is then capped and placed in a clay cylinder, and heated for about ten minutes by a low, flat flame, placed at considerable distance beneath. As soon as the odour of ammonia is no longer perceptible the nearly full flame of two Bunsen burners is applied, and continued for forty to fifty minutes. The sintered cake detaches readily from the crucible as a rule; if not, it is softened up in a few minutes by hot water and digested in a dish until thoroughly disintegrated. It is first washed by decantation, and any lumps are broken up by a pestle, then thrown on the filter and well washed with hot water. The residue should dissolve completely in hydrochloric acid without showing the least trace of unattacked mineral.

The calcium is separated at once by ammonia and ammonium carbonate, and again after evaporation of the filtrate and expulsion of ammonium chloride. The weighed alkaline chlorides should be dissolved in water and filtered before addition of platinic chloride, in order to correct for the few hundredths of a m.grm. of fixed residue which is invariably left on the filter.

If the rock contains sulphur this will in part be found with the alkaline chlorides as sulphate. Therefore, if the sulphur is at all considerable in amount, it must be removed by barium chloride before the second precipitation by ammonium carbonate; otherwise there is danger of the potassium platinic chloride carrying sodium sulphate. A faint reaction for sulphate can usually be obtained, anyway, if the evaporations have been made on a water-bath fed by gas.

Lithium.—After separation of the potassium platinic chloride, the alcoholic filtrate is evaporated and tested spectroscopically for lithium. This element is almost invariably present, but almost never in amount to warrant quantitative estimation. Should it be so, however, the excellent Gooch method (*Proc. Am. Acad. Arts Sci.*, p. 177, 1886; *Bull. U.S. Geol. Survey*, No. 42, p. 73, 1887; Chemical News, vol. lv., pp. 18, 29, 40, 56, 78, 1887) of separation by amyl alcohol is to be followed, after removal of the platinum by hydrogen gas.* In rock analysis there need be no fear of enough lithium remaining with the potassium to cause any concern.

For the most accurate work it is still necessary to look for, and if possible estimate, the few hundredths of a m.grm. of calcium chloride that may be with the sodium chloride.

Carbon Dioxide.

For this estimation an apparatus permanently set up is used, of which several forms have been described by different writers. The rock powder is boiled with dilute hydrochloric acid in a small Erlenmeyer flask, attached to an upward-inclined condenser, whence, after passing through a compact arrangement of drying tubes—first, one of calcium chloride, then one of andydrous copper sulphate to retain hydrogen sulphide from decomposable sulphides and any hydrochloric acid that may pass over, and finally a second calcium chloride tube—the carbon dioxide is retained by absorption tubes filled with soda lime followed by calcium chloride. Of course arrangement is made for a current of CO_2-free air with which to sweep out the apparatus before and after the experiment, and for a slow current during its continuance. The results are very accurate, and the determination can be quickly carried out.

In the preliminary qualitative test for carbon dioxide, it must be remembered that while calcite gives off its carbon dioxide on treatment with cold acid, dolomite and siderite do not, and hence warming should not be omitted; otherwise, a few tenths per cent of carbon dioxide can very well be overlooked. Moreover, the powder should first be stirred up with a little hot water, to remove all entangled air which might otherwise appear to be carbon dioxide.

(To be continued).

CORRESPONDENCE.

SCIENCE AND ART DEPARTMENT EXAMINATION.

To the Editor of the Chemical News.

Sir,—For more than twenty years I have annually sent pupils in for some of these examinations, and, although

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* From the *Bulletin of the United States Geological Survey*, No. 148, p. 15, 1897.

* When haste is not an object, this way of removing platinum from the chlorides of the alkalis is by far the neatest and most satisfactory. The small flask containing the solution is placed in a water-bath and attached to a hydrogen generator. After expelling all air the flask is closed, without breaking connection with the generator, and left to itself, except for occasional light shaking up, till reduction is accomplished.

at times unable to understand the reason for the adoption of some of the regulations, this is the first time that I have ever ventured to call attention to one or two points connected with the working of the Department. Recently, as is well known, the system of payment which has hitherto been adopted has been altered. It is claimed that this alteration is an improvement, because it is said to substitute payment by attendance for payment by results; but in reality it does nothing of the kind, for the examinational results are still one of the chief—if not *the* chief—factors in fixing the amount of grant. Also the amount of payment per attendance is so small that a most inadequate remuneration is given to the teacher. The result of this on the Science Classes throughout the country is that, while possibly only a comparatively slight alteration will be made in the total amount of money paid to large classes, such as the classes in large day-schools, the amount paid to smaller classes—especially those held in the evening where higher work is carried on—will be reduced to such an extent as to threaten the existence of many of them. For example, in a class known to me where work of the highest kind is carried on, and which work has been specially commended by the Inspector in two of his Annual Reports, the earnings this season will be reduced 75 per cent. If this is the outcome of the new policy, the sooner the Department reverts to the old plan the better for all concerned, and especially for the propagation of scientific knowledge.

Of course all teachers are aware of the anomalies which occur in examinations, but the following is a somewhat remarkable instance:—A student sat for the examination in May last in the Advanced Stage of Practical Organic Chemistry. He had to answer two questions and to analyse two substances (unknown), as well as to find the halogen element present in an organic solid and to determine the melting-point of this solid. The written questions were correctly answered, the analyses were correctly done, the halogen was correctly determined, and the melting-point of the substance was less than 1 per cent too low. The description of the practical work also was fairly well done; but this student is returned as having failed, notwithstanding that there are two classes of success—1st and 2nd class. It would be interesting to know, in the face of this, the standard the examiners require for a 1st class success. At the last May examinations the other chemistry results show many anomalies of a somewhat similar character.—I am, &c.,

D.Sc. (Lond.).

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvi., No. 23, June 6, 1898.

Yttric Earths contained in the Monazite Sands.—O. Boudouard.—Already inserted in full.

The Carbonic Acid of the Atmosphere.—MM. Albert-Lévy and H. Henriet.—The authors have made a daily examination of the atmospheric carbonic acid for the last twenty years, and they show that the loss pointed out by M. Gautier due to what escapes from the potash is but a negligible quantity; they have always maintained that baryta is far the best absorbent of carbonic acid, and by making two estimations simultaneously with potash and baryta they have arrived at some very interesting results. On the outskirts of Paris they got practically the same results in each case, but in the city of Paris baryta gives a decidedly higher figure.

On a Crystallised Heptacetine, a Derivative of Ouabaine.—M. Arnaud.—250 grms. of pure acetic anhydride is used to dissolve 5 grms. of $ZnCl_2$; after cooling we add all at once 25 grms. of finely powdered anhydrous ouabaine (dried for 24 hours at 110°). Heat gently to about 30°—35° to help the reaction; the temperature suddenly and spontaneously rises to 70°—75°, the ouabaine is rapidly dissolved, and the solution takes a brown colour, becoming perfectly clear; if the temperature sinks below 60° the solution must be gently heated to bring it up to 70° again; finally, after cooling, it is poured into five or six times its volume of warm water. On standing the insoluble acetine is deposited in a crystalline mass, which can be purified by dissolving in boiling alcohol at 85°. The return of crystallised acetine is about 50 per cent of the ouabaine used, for at the same time a large proportion of amorphous acetine is formed soluble in alcohol and in other solvents. Crystallised acetine possesses the glucoside function and is a derivative of ouabaine and not a product of its splitting up. Analytical results show that heptacetine is formed by the dehydration of ouabaine, which by etherification gives heptacetine—

$$C_{30}H_{37}(C_2H_3O)_7O_{11}.$$

Some Acetals of Pyrocatechin.—Ch. Moureu.—Following up his research on pyrocatechin it occurred to the author to try what would be the action exerted on the acetal function by the free phenol function in the still unknown oxyacetal-phenol, and also whether the ortho-position of this latter would favour the reaction. He found that the influence of the free phenol function on the acetal function leads to the production of a mixed acetal with a closed hexagonal chain, this last compound being capable of opening its chain by hydration with the formation of the aldehyd corresponding to the primitive oxyacetal-phenol.

Nitration of Cellulose and of its Hydro- and Oxy-derivatives.—Leo Vignon.—The author has submitted pure cotton cellulose and the hydro- and oxy-celluloses to nitration. The nitration was pushed to its maximum, so as to decide whether the number of etherifiable hydroxyls of the cellulose had undergone any modification by its transformation into hydro- and oxy-cellulose. Ten grms. of dried cellulose, hydrocellulose, and oxycellulose were immersed respectively in 150 c.c. of a mixture of—

H_2SO_4,	density 1·84..	3 parts
HNO_3,	,, 1·50..	1 part

The temperature was kept at 10° for twenty-four hours; the substance was then precipitated in two litres of cold water, washed till neutral, dried, and weighed; practically equal weights of the three substances were obtained—14 grms. to 16 grms. These nitrated products are inflammable; when kept in air the nitrated hydrocellulose becomes yellow and decomposes; so does the nitrated oxycellulose, but more slowly, while the nitrocellulose remains stable. The author concludes that cellulose, in its transformation into hydro- and oxy-cellulose, has not undergone any considerable change in the elementary structure of its original chemical type. It has, so to say, only been subjected to partial modifications, which form the subject of further research.

MISCELLANEOUS.

Schools of Chemistry, &c.—The following information was received too late for insertion in the "Students' Number":—

Sheffield Technical School (University College, Technical Department).—Professor of Metallurgy, J. O. Arnold; Lecturer, A. McWilliam, A.R.S.M.; Demonstrator and Lecturer on Fuel, F. K. Knowles; Lecturer in Chemistry, F. Ibbotson, B.Sc., F.C.S. The work is divided into two departments:—I. The Technical Department of the University College, including Mechanical, Electrical, Civil, and Mining Engineering; Metallurgy. II. The Evening Department, for providing Technical Instruction for persons engaged during the day in the local industries. The courses of Evening instruction include Magnetism and Electricity, Inorganic Chemistry, Experimental Laboratory, and Electrical Engineering. The Metallurgical Department has been equipped with a view to thoroughly meeting the requirements of the local industries. The Laboratory is fitted with the most modern apparatus for metallurgical analysis, more especially with appliances for the rapid and accurate chemical examination of Iron and Steel, Fuel, and Refractory materials. It also contains a complete pyrometric installation, and a new laboratory for the study of the micrographic analysis of metals has been completed and fully equipped with specially designed microscopes, by Ross, polishing tables, driven by an electric motor, etching appliances, incandescent light for evening work, &c. The School is now the most complete of its kind for teaching the practical manufacture, the chemical constitution, and the physical properties of steel. Special attention is given to the determination of the microscopic constituents of steel. Although the chief industry of the district occupies the central position in the course of instruction, general metallurgy is not neglected, but is dealt with in a separate syllabus, dealing with metals (other than iron and steel) used in the arts. Students are thus enabled to select and at once enter upon a course of scientific metallurgical training of immediate practical utility. They may take up and work through any portions of the course, but certificates will be granted only to those who follow the prescribed courses and pass the necessary examinations. The course of study is as follows:—Preparatory Chemistry, Metallurgy Lectures, Fuel Lectures, Practical Metallurgy, Practical Fuel Course, Geology and Mineralogy, and Electro-Metallurgy.

British Association for the Advancement of Science.—The following are the names of the Officers and Committee of Section B (Chemical Science) at the Bristol Meeting of the British Association:—

President—Professor F. R. Japp, F.R.S.

Vice-Presidents—W. Shenstone, F.R.S.; Professor E. Noelting; A. Vernon Harcourt, F.R.S.; J. H. Gladstone, F.R.S.; Professor W. Ramsay, F.R.S.; Professor Emerson Reynolds, F.R.S.; W. J. Russell, F.R.S.

Secretaries—C. A. Kohn (Recorder); F. Wallis Stoddart; T. K. Rose.

Committee—Professor H. E. Armstrong, F.R.S.; The Earl of Berkeley; C. H. Bothamley; Professor Clowes; Sir William Crookes, F.R.S.; Professor H. B. Dixon, F.R.S.; R. G. Durrant; W. J. Elliot; T. Fairley; F. Francis; G. Gladstone; Herbert Jackson; H. C. Jenkins; A. P. Laurie; C. H. Luxmoore; H. G. Madan; Hugh Marshall; Professor McLeod, F.R.S.; Professor Meldola, F.R.S.; H. Forster Morley; D. H. Nagel; A. C. Pass; H. Ramage; S. Rideal; Professor Roberts-Austen, F.R.S.; Professor Smithells; Professor Lloyd Snape; J. Spiller; A. Stansfield; W. H. Symons; Morris Travers; T. Turner; G. Ward; Professor R. Warington, F.R.S.; Professor Wertheimer; Professor Sydney Young, F.R.S.

The Papers brought before the Section were as follows:—

President's Address.—Stereochemistry and Vitalism.

Prof. W. Ramsay and Dr. Morris W. Travers—On the Extraction from Air of the Companions of Argon and on Neon.

Prof. J. Emerson Reynolds—On the Position of Helium, Argon, Krypton, &c., in the Periodic Classification of the Elements.

Report of the Committee on the Electrolytic Methods of Quantitative Analysis.

Dr. Hugh Marshall—A New Form of Stand for Electrolytic Analysis.

Report of the Committee on the Continuation of th Bibliography of Spectroscopy.

Prof. Sydney Young—Some Researches on the Thermal Properties of Gases and Liquids.

Dr. W. J. Russell—The Action exerted by certain Metals and Organic Substances on a Photographic Plate.

Prof. P. F. Frankland—The Action of Bacteria on Photographic Plates.

Dr. J. H. Gladstone and Mr. Hibbert—Further Experiments on the Absorption of the Röntgen Rays by Chemical Compounds.

Report of the Committee on the Action of Light upon Dyed Colours.

H. P. Laurie and E. H. Strange—The Cooling Curves of Fatty Acids.

Earl of Berkeley—On the More Exact Determination of the Densities of Crystals.

Prof. F. Clowes—The Equivalent Replacement of Metals.

Prof. W. R. Hodgkinson and A. H. Coote—A Note on the Alkaline Chlorates and Sulphates of Heavy Metals.

Joint Discussion with Section A.—The Recent Eclipse Expeditions.

Report of the Committee on the Teaching of Natural Science in Elementary Schools.

Prof. H. E. Armstrong—Juvenile Research.

R. G. Durrant—Green Cobaltic Compounds.

Dr. C. M. Luxmoore—The Analysis of Dorsetshire Soils.

Report of the Committee on the Carbohydrates of the Cereal Straws.

Report of the Committee on the Promotion of Agriculture.

Dr. J. G. Parker—Recent Advances in the Tanning Industry.

Prof. E. Noelting—A New Class of Colouring Matters; Amidated Aromatic Amidines.

J. H. Fenton and F. Jackson—The Oxidation of Glycerol in presence of Ferrous Iron.

Dr. R. S. Morrell and J. M. Croft—Action of Hydrogen Peroxide on Carbohydrates in presence of Iron Salts.

Prof. J. Emerson Reynolds—An Experiment illustrating the Effect on the Acetylene Flame of varying proportions of Carbon Dioxide in the Gas.

A. G. Vernon Harcourt—On a 10-candle Lamp to be used as a Standard of Light.

A. G. Vernon Harcourt—On a Convenient Form of Drying Tube.

Dr. S. Rideal—Standards of Purity for Sewage Effluents.

Prof. W. R. Hodgkinson and Capt. Owen—Action of Ammonia on Gun-cotton.

J. A. Smythe—Nitroso-pinene.

J. B. Wood, W. H. Spivey, and T. H. Easterfield—The Constitution of Oxycannabin.

C. H. Bothamley—The Action of certain Substances on the Undeveloped Photographic Image.

Report of the Committee on Preparing a New Series of Wave-length Tables of the Spectra of the Elements.

Report of the Committee on Isomeric Naphthalene Derivatives.

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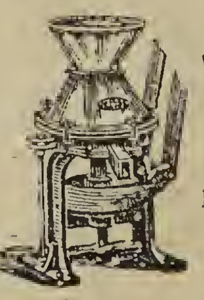

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THE CHEMICAL NEWS.

Vol. LXXVIII., No. 2026.

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION.

Bristol, 1898.

By Professor F. R. JAPP, M.A., LL.D., F.R.S., President of the Section.

(Concluded from p. 144).

These observations possibly afford a clue to the mode of action of the living organism in producing single enantiomorphs. This production of single asymmetric forms may be a result of the asymmetric character of the chemical compounds of which the tissues of plants and animals are built up. The optically active products of the organism —the carbohydrates, the terpenes, tartaric acid, asparagine, quinine, the serum of the blood, and countless others—have been formed in an asymmetric environment, and their asymmetry is an induced phenomenon. They have been cast, as it were, in an asymmetric mould. According to this view they are a result of the selective production of one of the two possible enantiomorphous forms. The same would hold good with regard to the organised tissues themselves, developed from inherited asymmetric beginnings in the ovum or the seed, or obtained by fission. The perplexing question of the *absolute origin* of these asymmetric compounds I will discuss later.

Another view has been put forward by Emil Fischer. In his lecture on "Syntheses in the Sugar Group," delivered before the German Chemical Society in 1890, he says:—

"Starting with formaldehyd, chemical synthesis leads, in the first instance, to the optically inactive acrose. In contradistinction to this only the active sugars of the *d*-mannitol series have hitherto been found in plants.

"Are these the only products of assimilation [of carbon dioxide and water]? Is the preparation of optically active substances a prerogative of the living organism; is a special cause, a kind of vital force, at work here? I do not think so, and incline rather to the view that it is only the imperfection of our knowledge which imports into this process the appearance of the miraculous.

"No fact hitherto known speaks against the view that the plant, like chemical synthesis, first prepares the inactive sugars; that it then resolves them into their active constituents, using the members of the *d*-mannitol series in building up starch, cellulose, inulin, &c., whilst the optical isomerides serve for other purposes at present unknown to us."

There are, therefore, two opposite processes which would account for the presence of optically active compounds among the substances generated in the living organism, and which we may briefly describe as *selective production* and *selective consumption*. An instance of artificial selective production is the formation of only one nitrile of *d*-mannoheptonic acid already cited. Selective consumption, dissociated, however, from the previous production of the racemoid form, may be illustrated by the fermentation of dextro-tartaric acid in the action, studied by Pasteur and already referred to, of a mould on racemic acid, the lævo-tartaric acid remaining untouched, and by numerous similar fermentations since discovered. Selective consumption is not restricted to living ferments; various cases are known of enzymes, or soluble ferments, which can effect the hydrolysis of one glucoside, but not of its enantiomorph. As Emil Fischer, who studied this phenomenon, says:—"Enzyme and glucoside must fit each other like key and lock, in order that the one may exercise a chemical action on the other." And a similar selective action, embracing the much more complex phenomenon of alcoholic fermentation, is displayed by E. Buchner's soluble zymase obtained from yeast cells.

It is true, moreover, that the organism sometimes produces both enantiomorphs. Thus the lactic ferment converts carbohydrates into racemoid lactic acid; ordinary, or lævo-rotatory, asparagine is accompanied in plants, as Piutti showed, by a small quantity of its optical isomeride; and there are other cases.

These facts might be taken as evidence in favour of Fischer's view that selective consumption is the cause of the phenomenon we are discussing. But I do not think that, in the present state of our knowledge, we can decide between the two views. For that matter both may be correct, each may explain particular cases. What I wish to point out is that Fischer's statement that the "miraculous" character of the phenomenon is eliminated by his assumption appears open to question. It is just as much, or as little, miraculous after as before. The production of a single asymmetric form, and the destruction of one of two opposite asymmetric forms, are problems of precisely the same order of difficulty, and there are only two ways in which either of them have ever been solved; firstly, by the direct action of living matter, and, secondly, by the use of previously existing asymmetric non-racemoid compounds, which are, in the last resort, due to the action of life. Directly, or indirectly, then, life intervenes.

Doubtless this will appear a very extraordinary statement in view of Jungfleisch's synthesis of racemic acid and its re-solution into dextro- and lævo-tartaric acids by the crystallisation of the sodium ammonium salts. The process does not take place in a living organism; nor is the aid of life invoked in the shape of a micro-organism as in Pasteur's third method of separation. No asymmetric base of vegetable origin is employed as in Pasteur's second method, so that the indirect action of life through its products is also excluded; sodium and ammonium are symmetric inorganic radicles, and no substance of one-sided asymmetry is introduced from beginning to end. The process is one of ordinary crystallisation: the two forms are deposited side by side, the operator afterwards picking out the right and left crystals and separating them. The reason why the two tartrates crystallise out and not the racemate, is that at the ordinary temperature of the air at which the crystallisation is conducted they are less soluble than the racemate. At a higher temperature, on the other hand, these solubilities are reversed and the racemate is deposited. The conditions are precisely those which govern the formation or non-formation of ordinary double salts.

Consequently the overwhelming majority of chemists hold that the foregoing synthesis and separation of optically active compounds have been effected without the intervention of life, either directly or indirectly. Every manual of stereochemistry emphasises this point.

I have already hinted that I hold a contrary opinion. I have held it for some time, but have not ventured to give public expression to it, except in lecturing to my students. I was deterred chiefly by the impression that I stood alone in my belief. I find, however, that this was a mistaken impression. In a lecture on "Pasteur as the Founder of Stereochemistry," which Professor Crum Brown delivered before the Franco-Scottish Society in July, , 1897, and which is published in the *Revue française d'Edimbourg*, he says, referring to the separation of enantiomorphs by crystallisation:—

"The question has often occurred to me: Do we here get rid of the action of a living organism? Is not the observation and deliberate choice by which a human being picks out the two kinds of crystals and places each in a vessel by itself the specific act of a living organism of a kind not altogether dissimilar to the selection made by *Penicillium glaucum*? But I do not insist on this, although I think it is not unworthy of consideration."

It is this question, so precisely posed by Professor Crum Brown, that I would discuss in detail. I think we shall find that the answer to it will be in the sense which he indicates. The action of life, which has been excluded during the previous stages of the process, is introduced the moment the operator begins to pick out the two enantiomorphs.

It will doubtless be objected that, if this is the case, there can be no such thing as a synthesis of a naturally occurring organic compound without the intervention of life, inasmuch as the synthetic process is always carried out by a living operator.

Here, however, we must draw an important distinction. In the great majority of the operations which we carry out in our laboratories—such as solution, fusion, vaporisation, oxidation, reduction and the like—we bring to bear upon matter symmetric forces only—forces of the same order as those involved in the chance motions of the molecules of a liquid or a gas. All such processes, therefore, might conceivably take place under purely chance conditions, without the aid of an operator at all. But there is another class of operations to which Pasteur first drew attention, those into which one-sided asymmetry enters, and which deal either with the production of a single enantiomorph, or with the destruction (or change) of one enantiomorph in a mixture of both, or with the separation of two enantiomorphs from one another. We have already seen that such processes are possible only under one-sided asymmetric influences, which may take the form either of the presence of an already existing enantiomorph, or of the action of a living organism, or of the free choice of an intelligent operator. They cannot conceivably occur through the chance play of symmetric forces.

We must, therefore, in classifying the actions of the intelligent operator, distinguish between those actions in which his services might conceivably be dispensed with altogether, and those in which his intelligence is the essential factor. To the former class belongs the carrying out of symmetric chemical reactions; to the latter, the separation of enantiomorphs.

Take the synthesis of formic acid—a symmetric compound—by the absorption of carbon monoxide by heated caustic alkali. Given a forest fire and such naturally occurring materials as limestone, sodium carbonate, and water, it would not be difficult to imagine a set of conditions under which a chance synthesis of sodium formate from inorganic materials might occur. I do not assert that the conditions would be particularly probable, still they would not be inconceivable. But the chance synthesis of the simplest optically active compound from inorganic materials is absolutely inconceivable. So also is the separation of two crystallised enantiomorphs under purely symmetric conditions.

The picking out of the two enantiomorphs is, moreover, to be distinguished from the process of similarly separating the crystals of two different non-enantiomorphous substances, although this distinction is commonly ignored by classing both processes together as *mechanical*, in opposition to *chemical* separations. In the case of the non-enantiomorphs there may be differences of solubility, of specific gravity and the like, so that other means of separation, involving only the play of symmetric forces, may be resorted to. Such a process may justly be regarded as "mechanical." But the two crystallised enantiomorphs, as we have seen, have the same solubility—at least in symmetric solvents, the same specific gravity, behave, in fact, in an indentical manner towards all symmetric forces, so that no separation by such means is feasible. It requires the living operator, whose intellect embraces the conception of opposite forms of asymmetry, to separate them. Such a process cannot, by any stretch of language, be termed "mechanical." Conscious selection here produces the same result as the unconscious selection exercised by the micro-organism, the enzyme, or the previously existing asymmetric compound.

I need not point out that if the operator chooses to bring about the separation by an asymmetric solvent, or some other asymmetric means, he is still making use of his conception of asymmetry. He merely effects his end indirectly instead of directly. But in either case he exercises a guiding power which is akin, in its results, to that of the living organism, and is entirely beyond the reach of the symmetric forces of inorganic nature.

In like manner it is not of the least consequence, for the purposes of the present argument, whether the micro-organism, with which we have compared the operator, acts directly in fermenting one of two enantiomorphs, or whether it acts indirectly by first preparing an asymmetric enzyme which displays this selective action. The contention, therefore, of E. Fischer, Buchner, and others, that the discovery of enzymes and zymases "has transferred the phenomena of fermentation from biological to purely chemical territory," is true only as regards the immediate process, and leaves intact the *vitalistic origin* of these phenomena.

We thus arrive at the conclusion that the production of single asymmetric compounds, or their isolation from the mixture of their enantiomorphs, is, as Pasteur firmly held, the prerogative of life. Only the living organism with its asymmetric tissues, or the asymmetric products of the living organism, or the living intelligence with its conception of asymmetry, can produce this result. Only asymmetry can beget asymmetry.

Is the failure to synthesise single asymmetric compounds without the intervention, either direct or indirect, of life, due to a permanent inability, or merely to a temporary disability which the progress of science may remove? Pasteur took the latter view, and suggested that the formation of chemical compounds in the magnetic field, or under the influence of circularly polarised light, would furnish a means of solving the problem; and van 't Hoff also thinks the latter method feasible. As regards magnetism Pasteur's suggestion was undoubtedly based on a misconception; the magnetic field has not an asymmetric structure; it is merely polar, since the rotation which it produces in the plane of polarisation of a ray of light changes sign with the direction of the field. As regards circularly polarised light I must confess to having doubts as to whether it can be regarded as an asymmetric phenomenon: the motion of the ether about the axis of the ray is circular, not spiral, and it is only by considering the difference of phase from point to point along the ray that the idea of a spiral can be evolved from it. In fact, are there such things as forces asymmetric in themselves? Is the geometrical conception of asymmetry applicable to dynamical phenomena at all, except in so far as these deal with asymmetric material structures, such as quartz crystals, or organic molecules containing asymmetric carbon atoms? But this is a question which I would submit to the judgment of mathematical physicists.

One thing is certain—namely, that all attempts to form optically active compounds under the influence of magnetism or circularly polarised light have hitherto signally failed. These forces do not distinguish between the two equally exposed points of attack which present themselves in the final stage of the transformation of a symmetric into an asymmetric carbon atom.

But even if such an asymmetric force could be discovered—a force which would enable us to synthesise a single enantiomorph—the process would not be free from the intervention of life. Such a force would necessarily be capable of acting in two opposite asymmetric senses; left to itself it would act impartially in either sense, producing, in the end, both enantiomorphs in equal amount. Only the free choice of the living operator could direct it consistently into one of its two possible channels.

I will briefly recapitulate the conclusions at which we have arrived. Non-living, symmetric matter—the matter of which the inorganic world is composed—interacting under the influence of symmetric forces to form asymmetric compounds, always yields either pairs of enantiomorphous molecules (racemoid form), or pairs of enantiomorphous groups united within the molecule (meso-form), the result being, in either case, mutual compensation and consequent optical inactivity. The same will hold good of symmetric matter interacting under the influence of asymmetric forces (supposing that such forces exist), provided that the latter are left to produce their effect under conditions of pure chance.

If these conclusions are correct, as I believe they are, then the *absolute origin* of the compounds of one-sided asymmetry to be found in the living world is a mystery as profound as the absolute origin of life itself. The two phenomena are intimately connected, for, as we have seen, these symmetric compounds make their appearance with life, and are inseparable from it.

How, for example, could lævo-rotatory protein (or whatever the first asymmetric compound may have been) be spontaneously generated in a world of symmetric matter, and of forces which are either symmetric or, if asymmetric, are asymmetric in two opposite senses? What mechanism could account for such selective production? Or if, on the other hand, we suppose that dextro- and lævo-protein were simultaneously formed, what conditions of environment existing in such a world could account for the survival of the one form and the disappearance of the other? Natural selection leaves us in the lurch here, for selective consumption is, under these conditions, as inconceivable as selective production.

No fortuitous concourse of atoms, even with all eternity for them to clash and combine in, could compass this feat of the formation of the first optically active organic compound. Coincidence is excluded, and every purely mechanical explanation of the phenomenon must necessarily fail.

I see no escape from the conclusion that, at the moment when life first arose, a directive force came into play—a force of precisely the same character as that which enables the intelligent operator, by the exercise of his Will, to select one crystallised enantiomorph and reject its asymmetric opposite.

I would emphasise the fact that the operation of a directive force of this nature does not involve a violation of the law of the conservation of energy. Enantiomorphs have the same heat of formation; the heat of transformation of one form into the other is nil. Whether, therefore, one enantiomorph alone is formed, or its optical opposite alone, or a mixture of both, the energy required per unit weight of substance is the same. There will be no dishonoured drafts on the unalterable fund of energy.

The interest of the phenomena of molecular asymmetry from the point of view of the biologist lies in the fact that they reduce to its simplest issues the question of the possibility or impossibility of living matter originating from dead matter by a purely mechanical process. They reduce it to a question of solid geometry and elementary dynamics; and therefore if the attempted mechanical explanation leads to a *reductio ad absurdum*, this ought to be of a correspondingly simple and convincing character. Let us see how far this is the case.

Life is a phenomenon of bewildering complexity. But in discussing the problem of the origin of life, this complexity cuts two ways. Whilst, on the one hand, it is appealed to by one set of disputants as an argument against the mechanical theory, on the other it affords shelter for the most unproved statements of their opponents. I will take a concrete instance from the writings of an upholder of the mechanical theory of the origin of life, the late Professor W. K. Clifford. He says:

"Those persons who believe that living matter, such as protein, arises out of non-living matter in the sea, suppose that it is formed like all other chemical compounds. That is to say it originates in a coincidence, and is preserved by natural selection. . . . The coincidence involved in the formation of a molecule so complex as to be called *living* must be, so far as we can make out, a very elaborate coincidence. But how often does it happen in a cubic mile of sea water? Perhaps once a week; perhaps once in many centuries; perhaps, also, many million times a day. From this living molecule to a speck of protoplasm visible in the microscope is a very far cry; involving, it may be, a thousand years or so of evolution."

It was easy for Clifford to write thus concerning life itself, for it was difficult for any one to contradict him. But had he been asked whether any mechanical (symmetric) coincidence would suffice to convert an infinitely great number of molecules of the type shown in fig. 3 into that shown in (say) fig. 1, to the exclusion of that shown in fig. 2; or whether, given a mixture, in equal proportions, of molecules of the types shown in figs. 1 and 2, any mechanical (symmetric) conditions of environment would bring about the destruction of one kind and the survival of the other, I think his exact mathematical and dynamical knowledge would have prevented him from giving an affirmative answer. But short of this affirmative answer, his other statements, it seems to me, fall to the ground.

I am convinced that the tenacity with which Pasteur fought against the doctrine of spontaneous generation was not unconnected with his belief that chemical compounds of one-sided asymmetry could not arise save under the influence of life.

Should any one object that the doctrine of the asymmetric carbon atom is a somewhat hypothetical foundation on which to build such a superstructure of argument as the foregoing, I would point out that the argument is in reality independent of this doctrine. All that I have said regarding the *molecular* asymmetry of naturally occurring optically active organic compounds, and all the geometrical considerations based thereon, hold good equally of the hemihedral *crystalline* forms of these compounds, about which there is no hypothesis at all. The production of a compound crystallising in one hemihedral form to the exclusion of the opposite hemihedral form, as in the case of the tartaric acid of the grape, is a phenomenon inexplicable on the assumption that merely mechanical, symmetric forces are at work. Nor is this conclusion invalidated even if we ultimately have to admit that the connection between molecular and crystalline asymmetry is not an invariable one—a point about which there is some dispute.

At the close of the lectures from which I have so frequently quoted, Pasteur, with full confidence in the importance of his work, but without any trace of personal vanity, says:—

"It is the theory of molecular asymmetry that we have just established—one of the most exalted chapters of science. It was completely unforeseen, and opens to physiology new horizons, distant but sure."

I must leave physiologists to judge how far they have availed themselves of the new outlook which Pasteur opened up to them. But if I have in any way cleared the view towards one of these horizons, I shall feel that I have not occupied this chair in vain.

Some of my hearers, however, may think that, instead of rendering the subject clearer, I have brought it perilously near to the obscure region of metaphysics; and certainly, if to argue the insufficiency of the mechanical explanation of a phenomenon is to be metaphysical, I must plead guilty to the charge. I will, therefore, appeal to a judgment—metaphysical, it is true, but to be found in a very exact treatise on physical science—namely, Newton's "Principia." It has a marked bearing on the subject in hand:—

"*A cæca necessitate metaphysica, quæ utique eadem est semper et ubique, nulla oritur rerum variatio.*"

I will merely add that this is certainly true of the particular *rerum variatio* in which optically active organic compounds originate.

ADDRESS TO THE MATHEMATICAL AND PHYSICAL SECTION OF THE BRITISH ASSOCIATION.

Bristol, 1898.

By Professor W. E. AYRTON, F.R.S.,
President of the Section.

A year ago Section A was charmed with a Presidential Address on the poetry of mathematics, and if, amongst those who entered the Physics lecture theatre at Toronto on that occasion, there were any who had a preconceived notion that mathematics was a hard, dry, repellent type of study, they must, after hearing Professor Forsyth's eloquent vindication of its charms, have departed convinced that mathematics resembled music in being a branch of the fine arts. Such an address, however, cannot but leave a feeling of regret amongst those of us who engulfed in the whirl of the practical science of the day, sigh for the leisure and the quiet which are necessary for the worship of abstract mathematical truth, while the vain effort to follow in the footsteps of one gifted with such winning eloquence fills me with hopeless despair.

Section A this year is very fortunate in having its meetings associated with those of an "International Conference on Terrestrial Magnetism and Atmospheric Electricity," which is attended by the members of the "Permanent Committee for Terrestrial Magnetism and Atmospheric Electricity" of the "International Meteorological Conference." It has been arranged that this Permanent Committee, of which Professor Rücker is the President, shall form part of the General Committee of Section A, and also shall act as the Committee of the International Conference, which will itself constitute a separate department of Section A. For the purpose, however, of preparing a Report to the International Meteorological Conference, and for similar business, this Permanent Committee will act independently of the British Association.

My first duty to-day, therefore, consists in expressing the honour and the very great pleasure which I feel in bidding you, members of the International Conference, most heartily welcome.

Among the various subjects which it is probable that the Conference may desire to discuss, there is one to which I will briefly refer, as I am able to do so in a triple capacity. The earth is an object of much importance, alike to the terrestrial magnetician, the telegraph electrician, and the tramway engineer; but while the first aims at observing its magnetism, and the second rejoices in the absence of the earth currents which interfere with the sending of messages, the third seems bent on converting our maps of lines of force into maps of lines of tramway.

It might, therefore, seem as if electric traction—undoubtedly a great boon to the people, and one that has already effected important social developments in America and on the continent of Europe—were destined in time to annihilate magnetic observatories near towns, and even to seriously interfere with existing telegraph and telephone systems. Already the principle of the survival of the fittest is quoted by some electrical engineers, who declare that if magnetic observatories are crippled through the introduction of electric tramways, then so much the worse for the observatories. And I fear that my professional brethren only look at me askance for allowing my devotion to the practical applications of electricity to be tainted with a keen interest in that excessively small, but none the less extremely wonderful, magnetic force which controls our compass needles.

But this interest emboldens me to ask again, Can the system of electric traction that has already destroyed the two most important magnetic observatories in the United States and British North America be the best and the fittest to survive? Again, do we take such care, and spend such vast sums, in tending the weak and nursing the sick because we are convinced that they are the fittest to survive? May it not perhaps be because we have an inherent doubt about the justness of the survival of the strongest, or because even the strongest of us feels compelled to modestly confess his inability to pick out the fittest, that modern civilisation encourages *not* the destruction but the preservation of what has obvious weakness, on the chance that it may have unseen strength?

When the electrical engineer feels himself full of pride at the greatness, the importance, and the power of his industry, and when he is inclined to think slightingly of the deflection of a little magnet compared with the whirl of his 1000 horse-power dynamo, let him go and visit a certain dark store-room near the entrance hall of the Royal Institution, and, while he looks at some little coils there, ponder on the blaze of light that has been shed over the whole world from the dimly-lighted cupboard in which those dusty coils now lie. Then he may realise that while the earth as a magnet has endured for all time, the earth as a tramway conductor may at no distant date be relegated to the class of temporary makeshifts, and that the raids of the feudal baron into the agricultural fields of his neighbours were not more barbarous than the alarms and excursions of the tramway engineer into the magnetic fields of his friends.

A very important consideration in connection with the rapid development of physical inquiry is the possibility of extending our power of assimilating current physical knowledge. For so wide have grown the limits of each branch of physics that it has become necessary to resort to specialisation if we desire to widen further the region of the known. On the other hand, so interlinked are all sections of physics that this increase of specialisation is liable to hinder rather than assist advance of the highest order.

An experimenter is, therefore, on the horns of a dilemma—on the one hand, if he desires to do much he must confine himself more or less to one line of physical research, while, on the other hand, to follow that line with full success requires a knowledge of the progress that is being made along all kindred lines. Already an investigator who is much engaged with research can hardly do more as regards scientific literature than read what he himself writes—soon he will not have time to do even that. Division of labour and co-operation have, therefore, become as important in scientific work as in other lines of human activity. Like bees, some must gather material from the flowers that are springing up in various fields of research, while others must hatch new ideas. But, unlike bees, all can be of the "worker" class, since the presence of drones is unnecessary in the scientific hive.

Englishmen have long been at a disadvantage in not possessing any ready means of ascertaining what lines of physical inquiry were being pursued in foreign countries —or, indeed, even in their own. And, so far from making it easier to obtain this information, our countrymen have, I fear, until quite recently, been guilty of increasing the difficulty. For every college, every technical school in Great Britain—and their number will soon rival that of our villages—seems to feel it incumbent on itself to start a scientific society. And in accordance with the self-reliant character of our nation, each of these societies must be maintained in absolute independence of every other society, and its proceedings must be published separately, and in an entirely distinct form from those of any similar body. To keep abreast, then, with physical advance in our own country is distinctly difficult, while the impossibility of maintaining even a casual acquaintance with foreign scientific literature lays us open to a charge of international rudeness.

There is, of course, the German *Beiblätter*, but the

Anglo-Saxon race, which has spread itself over so vast a portion of the globe, is proverbially deficient in linguistic powers, and consequently, till quite recently, information that was accessible to our friends on the Continent was closed to many workers in Great Britain, America, and Australia.

Influenced by these considerations the Physical Society of London, in 1895, embarked on the publication of abstracts from foreign papers on pure physics, and, as it was found that this enterprise was much appreciated, the question arose at the end of the following year, whether, instead of limiting the journals from which abstracts were made to those appearing in foreign countries, and the papers abstracted to those dealing only with pure physics, the abstracts might not with advantage be enlarged, so as to present a *résumé* of all that was published in all languages on physics and its applications.

The first application of physics which it was thought should be included was electrical engineering, and so negotiations were opened with the Institution of Electrical Engineers. After much deliberation on the part of the representatives of the two societies, it was finally decided to start a monthly joint publication, under the management of a committee of seven, two of whom should represent the Institution of Electrical Engineers, two the Physical Society, and three the two societies jointly. *Science Abstracts* was the name selected for the periodical, and the first number appeared in January of this year.

A section is devoted to general physics, and a separate section to each of its branches; similarly a section is devoted to general electrical engineering, and a separate section to each of its more important subdivisions. The value of *Science Abstracts* is already recognised by the British Association as well as by the Institution of Civil Engineers, for those societies make a liberal contribution towards the expenses of publication, for which the Physical Society and the Institution of Electrical Engineers are responsible.

At no distant date it is thought that other bodies may co-operate with us, and we have hopes that finally the scheme may be supported by the scientific societies of many Anglo-Saxon countries. For our aim is to produce, in a single journal, a monthly record in English of the most important literature appearing in all languages on physics and its many applications. This is the programme—a far wider one, be it observed, than that of the *Beiblätter*—which we sanguinely hope our young infant *Science Abstracts* will grow to carry out.

The saving of time and trouble that will be effected by the publication of such a journal can hardly be overestimated, and the relief experienced in turning to a single periodical for knowledge that could hitherto be obtained solely by going through innumerable scientific newspapers, in many different languages, can only be compared with the sensation of rousing from a distracting and entangled dream to the peaceful order of wakeful reality.

I therefore take this opportunity of urging on the members of the British Association the importance of the service which they can individually render to science by helping on an enterprise that has been started solely in its aid, and not for commercial purposes.

The greatness of the debt owed by industry to pure science is often impressed on us, and it is pointed out that the comparatively small encouragement given by our nation to the development of pure science is wholly incommensurate with the gratitude which it ought to feel for the commercial benefits science has enabled it to reach. This is undoubtedly true, and no one appreciates more fully than myself how much commerce is indebted to those whose researches have brought them—it may be fame, but certainly nothing else. The world, however, appears to regard as equitable the division of reward which metes out tardy approbation to the discoverer for devising some new principle, a modicum of the world's goods to the inventor for showing how this principle can be applied, and a shower of wealth on the contractor for putting the principle into practice. At first sight this appears like the irony of fate, but in fact the world thus only proves that it is human by prizing the acquisition of what it realises that it stands in need of, and by valuing the possession of what it is able to comprehend.

Now is there not a debt which those who pursue pure science are in their turn equally forgetful of—viz., the debt to the technical worker or to some technical operation for the inception of a new idea? For purely theoretical investigations are often born of technics, or, as Whewell puts it, "Art is the parent, not the progeny, of science; the realisation of principles in practice forms part of the prelude as well as of the sequel of theoretical discovery." I need not remind you that the whole science of floating bodies is said to have sprung from the solution by Archimedes of Hiero's doubt concerning the transmutation of metals in the manufacture of his crown. In that case, however, it was the transmutation of gold into silver, and not silver into gold, that troubled the philosopher.

Again, in the "History of the Royal Society at the End of the Eighteenth Century," Thomson says regarding Newton, "A desire to know whether there was anything in judicial astrology first put him upon studying mathematics. He discovered the emptiness of that study as soon as he erected a figure; for which purpose he made use of one or two problems in Euclid. . . . . He did not then read the rest, looking upon it as a book containing only plain and obvious things."

The analytical investigation of the motion of one body round an attracting centre, when disturbed by the attraction of another, was attacked independently by Clairault, D'Alembert, and Euler, because the construction of lunar tables had such a practical importance, and because large money prizes were offered for their accurate determination.

The gambling table gave us the whole Theory of Probability, Bernoulli's and Euler's theorems, and the first demonstration of the binomial theorem, while a request made to Montmort to determine the advantage to the banker in the game of "pharaon" started him on the consideration of how counters could be thrown, and so led him to prove the multinomial and various other algebraical theorems. Lastly, may not the gambler take some credit to himself for the first suggestion of the method of least squares, and the first discussion of the integration of partial differential equations with finite differences contained in Laplace's famous "Théorie Analytique des Probabilités"?

The question asked Rankine by James R. Napier regarding the horse-power which would be necessary to propel, at a given rate, a vessel which Napier was about to build, resulted in the many theoretical investigations carried out by Rankine on water lines, skin-friction, stream lines, &c. For, as Professor Tait has said, "Rankine, by his education as a practical engineer, was eminently qualified to recognise the problems of which the solution is required in practice; but the large scope of his mind would not allow him to be content with giving merely the solution of those particular cases which most frequently occur in engineering as we now know it. His method invariably is to state the problem in a very general form, find the solution, and apply this solution to special cases."

Helmholtz studied physiology because he desired to be a doctor, then physics because he found that he needed it for attacking physiological problems, and lastly mathematics as an aid to physical research. But I need not remind you that it is his splendid work in mathematics, physics, and physiology, and not his success in ministering to the sick, that has rendered his name immortal.

Did not Kepler ask "How many would be able to make astronomy their business if men did not cherish the hope of reading the future in the skies?" And did he not warn those who objected to the degradation of mingling astrology with astronomy, to beware of "throwing away the child with the dirty water of its bath"? Even now, may we not consider all the astronomical research work done at the Royal Observatory, Greenwich, as a by-product, since the Observatory is officially maintained merely for the purposes of navigation? And are there not many of us who feel assured that, since researches in pure physics and the elucidation of new physical facts must quite legitimately spring from routine standardising work, the most direct way—even now at the end of the nineteenth century—of securing for the country a National Physical Laboratory is to speed forward a Government standardising institute?

Lastly, as you will find in Dr. Thorpe's fascinating "Life of Davy," it was the attempt to discover the medicinal effect of gases at the Pneumatic Institution in this city that opened up to Davy the charm of scientific research. And, indeed, the Royal Institution itself, the scientific home of Davy, Faraday, Tyndall, Rayleigh, and Dewar, owes its origin to Romford's proposal "for forming in London by private subscription an establishment for feeding the poor and giving them useful employment . . . connected with an institution for introducing and bringing forward into general use new inventions and improvements by which domestic comfort and economy may be promoted."

(To be continued).

ON THE EXTRACTION OF THE COMPANIONS OF ARGON AND ON NEON.*

By WILLIAM RAMSAY, F.R.S., and MORRIS W. TRAVERS.

In the Presidential Address to the Chemical Section of this Association, delivered last year at Toronto, it was pointed out that the densities of helium and argon being respectively 2 and 20 in round numbers, and the ratio of their specific heats being in each case 1·66, their atomic weights must be respectively 4 and 40. If the very probable assumption is made that they belong to the same group of elements, it appears almost certain on the basis of the Periodic Table that another element should exist, having an atomic weight higher than that of helium by about 16 units, and lower than that of argon by about 20. There is also room for elements of higher atomic weight than argon, belonging to the same series. The search for this element was described in last year's Address, and, it will be remembered, the results were negative.

Reading between the lines of the Address, an attentive critic might have noticed that no reference was made to the supposed homogeneity of argon. From speculations of Dr. Johnstone Stoney, it would follow that the atmosphere of our planet might be expected to contain new gases, if such exist at all, with densities higher than 8 or thereabouts. Dr. Stoney gives his reasons for supposing that the lighter the gas the less its quantity in our atmosphere, always assuming that no chemical compounds are known which would retain it on the earth, or modify its relative amount. Therefore it appeared worthy of inquiry whether it was possible to separate light and also heavy gases from argon.

The beautiful machine invented by Dr. Hampson has put it in our power to obtain, through his kindness and that of the "Brin" Oxygen Company, large quantities of liquid air. We were therefore able to avail ourselves of the plan of liquefaction, and subsequent fractional distillation, in order to separate the gases.

On liquefying 18 litres of argon, and boiling off the first fraction, a gas was obtained of density 17 (o = 16). This gas was again liquefied and boiled off in six fractions. The density of the lightest fraction was thus reduced to 13·4, and it showed a spectrum rich in red, orange, and yellow lines, differing totally from that of argon. On refractionating, the density was reduced further to 10·8; the gas still contained a little nitrogen, on removing which the density decreased to 9·76. This gas is no longer liquefiable at the temperature of air boiling under a pressure of about 10 m.m.; but if, after compression to two atmospheres, the pressure was suddenly reduced to about a quarter of an atmosphere, a slight mist was visible in the interior of the bulb. This gas must necessarily have contained argon, the presence of which would obviously increase its density; and in order to form some estimate of its true density, some estimate must be made of the relative amount of the argon. We have to consider a mixture of neon, nitrogen, and argon, the two latter of which are capable, not merely of being liquefied, but of being solidified without difficulty. Under atmospheric pressure nitrogen boils at −194°, and solidifies at −214°, and the boiling-point of argon is −187°, and the freezing-point −190°; the vapour-pressure of nitrogen is therefore considerably higher than that of argon. The mist produced on sudden expansion consisted of solid nitrogen and argon; and for want of better knowledge, assuming the vapour-pressure of the mixture of nitrogen and argon to be the sum of the partial pressures of the two, it is obvious that that of argon would form but a small fraction of the whole. The vapour-pressure of argon was found experimentally to be 109 m.m. at the temperature of air boiling in as good a vacuum as could be produced by our pump; but as we have only to consider the partial pressure of the argon at a much lower temperature, we do not believe that the pressure of the argon can exceed 10 m.m. in the gas. This would correspond to a density for neon of 9·6.

The ratio between the specific heat at constant pressure and constant volume was determined in the usual way for neon, and, as was to be expected, it approximates closely to the theoretical ratio, being 1·655. We therefore conclude that, like helium and argon, the gas is monatomic.

It may be remembered that the refractivity of helium compared with that of air is exceptionally low—viz., 0·1238. The lighter gas, hydrogen, has a refractivity of 0·4733. It was to be expected from the monatomic character and low density of neon that its refractivity should be also low; this expectation has been realised, for the number found is 0·3071. Argon, on the other hand, has a refractivity not differing much from that of air—viz., 0·958. Since the sample of neon certainly contains a small amount of argon, its true refractivity is probably somewhat lower. Experiments will be carried out later to ascertain whether neon resembles helium in its too rapid rate of diffusion.

The spectrum of neon is characterised by brilliant lines in the red, the orange, and the yellow. The lines in the blue and violet are few, and comparatively inconspicuous. There is, however, a line in the green, of approximate wave-length 5030, and another of about 5400.

A few words may be said on the other companions of argon. The last fractions of liquefied argon show the presence of three new gases. These are krypton, a gas first separated from atmospheric air, and characterised by two very brilliant lines, one in the yellow and one in the green, besides fainter lines in the red and orange; metargon, a gas which shows a spectrum very closely resembling that of carbon monoxide, but characterised by its inertness, for it is not changed by sparking with oxygen in presence of caustic potash; and a still heavier gas, which we have not hitherto described, which we propose to name "xenon." Xenon is very easily separated, for it possesses a much higher boiling-point, and remains behind after the others have evaporated. This gas, which has been obtained practically free from krypton, argon, and metargon, possesses a spectrum

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* A Paper read before the British Assocation (Section B), Bristol Meeting, 1898.

analogous in character to that of argon, but differing entirely in the position of the lines. With the ordinary discharge the gas shows three lines in the red, and about five very brilliant lines in the blue; while with the jar and spark-gap these lines disappear, and are replaced by four brilliant lines in the green, intermediate in position between the two groups of argon lines, the glow in the tube changing from blue to green. Xenon appears to exist only in very minute quantity.

Indeed all of these gases are present only in small amount. It is, however, not possible to state with any degree of accuracy in what proportion they are present in atmospheric argon. Of neon, perhaps, we may say that the last fraction of the lightest 100 c.c. from 18 litres of atmospheric argon no longer shows the neon spectrum, and possesses the density of argon; it may be safe to conclude, therefore, that 18 litres of argon do not contain more than 50 c.c. of neon; the proportion of neon in air must therefore be about one part in 40,000. We should estimate the proportion of the heavy gases at even less.

It follows from these remarks that the density of argon is not materially changed by separating from it its companions. A sample of gas, collected when about half the liquid argon or about 10 c.c. had boiled off, possessed the density 19·89; the density of atmospheric argon is 19·94. But, of course, we give this density of argon as only provisional (July 30, 1898); for a final determination the density must be determined after more thorough fractionation.

With a density of 9·6, and a consequent atomic weight of 19·2, neon would follow fluorine and precede sodium in the Periodic Table; as to the other gases, further research will be required to determine what position they hold.

EQUIVALENT REPLACEMENT OF METALS.*

By Professor **FRANK CLOWES**, D.Sc. (Lond.).

It has long been known that when iron is immersed in a solution of cupric sulphate metallic copper is deposited, and an amount of iron passes into solution which is exactly able to combine with the sulphate radicle liberated from the cupric sulphate. The weights of copper and of iron which combine with the same weight of sulphate radicle have been determined by carrying out the process quantitatively. These weights are chemically equivalent to one another, for they are able to combine with the same weight of the acidulous radicle.

In the case just cited, the chemical change appears at ordinary temperature and with dilute cupric solution, to follow the simple course stated. But attempts to extend this direct method of ascertaining the relative equivalents of metals cease to be direct in certain cases, owing to the complicated nature of the reactions which occur.

My attention was drawn to such a complication in the case of the action of magnesium on cupric sulphate solution, and the nature of the reaction was then investigated by R. M. Caven, B.Sc., and myself. Commaille (*Comptes Rendus*, lxiii., p. 556), Kern (Chem. News, xxxiii., p. 236), and Vitali (*Journ. Chem. Soc.*, lxx., 419), had drawn attention to the facts that during the action of magnesium on cupric sulphate solution cuprous oxide was deposited with the metallic copper, and hydrogen was evolved. These facts prove that the copper equivalent of magnesium cannot be obtained by simply weighing the magnesium which passes into solution and the deposit which was formed during the process. But we proceeded to make a fuller examination of the nature of the reaction, and to show that when it was quantitatively carried out the products enabled us to calculate the equivalents of magnesium and copper.

Having obtained practically pure materials, we proceeded to study the reactions when the conditions were varied by employing hot or cold and strong or weak cupric sulphate solutions. We were met with the initial difficulty that cupric sulphate solution deposits a basic salt when it is boiled: this salt we separated and found to correspond in composition and properties to the formula $4CuSO_4.7Cu(OH)_2.H_2O$. Pickering had separated a similar salt, to which he attributed the formula $6CuO.2SO_3.5H_2O$. Owing to the deposition of this salt complicating the products, we avoided actual ebullition in our experiments.

The action is most simple when the magnesium is immersed in a hot strong solution of cupric sulphate. Hydrogen is briskly evolved, a chocolate-coloured deposit forms, and green flakes are produced which disappear before the reaction is completed. Treatment of the brown deposit with dilute hydrochloric acid yields colourless cuprous chloride solution and a small residue of metallic copper. The hydrogen evolved was collected and measured, the metallic copper was weighed directly, and the amount of cuprous oxide was determined by dissolving it in hydrochloric acid and determining the amount of cuprous chloride thus formed by titrating it with standard permanganate solution in the presence of a sufficient amount of magnesium sulphate. As a result of four experiments the average sum of the magnesium equivalents of the cuprous oxide, the copper, and the hydrogen amounted to 0·102 grm., and the average weight of magnesium used was 0·105 grm. The ratios of the weights of hydrogen, copper, and cuprous oxide produced were constant only when the conditions of the experiment were precisely similar.

When the hot cupric sulphate is dilute, or when it is employed at ordinary temperature, the reaction pursues at first a similar course, but it soon becomes very considerably delayed by the formation of a green basic cupric salt, intermingled with colourless basic magnesium salt. Thus the reaction on the magnesium was usually complete in ten minutes in an excess of a hot strong solution of cupric sulphate; but in weak and cold solutions it often extended over several days, and even a week.

The percentage of hydrogen, compared with that which is equivalent to the magnesium employed, was in the case of the hot solution 34·7; with the cold solution it was 41·5 with weak solution, and 30·6 with saturated solution.

Various explanations have been given of the causes which lead to deposition of cuprous oxide and to evolution of hydrogen. It has been suggested that the change is due to impurity in the copper salt; this we have disproved by using a salt purified by frequent re-crystallisation, and yielding 25·23 per cent of copper (theory = 25·39); we have also proved the purity of the magnesium employed. Divers suggests that the evolution of hydrogen is due to the action of the magnesium upon free sulphuric acid, which has been formed by hydrolysis of the cupric salt. This seems to us to be an insufficient explanation of the rapidity with which hydrogen is evolved. Cold cupric sulphate solution was found to give no acid reaction with methyl-orange, although it is faintly acid to litmus paper. Yet such a solution gives an immediate evolution of hydrogen when magnesium is immersed in it, the evolution of the gas being very rapid in a hot and strong solution. After carefully studying the change, we are inclined to attribute the evolution of hydrogen in small degree to the presence of free sulphuric acid formed by hydrolysis in cold solution, and in greater degree to the same cause in hot solution. This involves the formation and separation of basic salt. This reaction, however, does not account for all the hydrogen evolved, and one of us will be prepared before long to advance a further explanation to account for this. Divers further suggests that cuprous sulphate is formed and almost immediately converted by the action of the basic cupric salt into cuprous oxide; this theory we also find to be untenable.

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* A Paper read before the British Association (Section B), Bristol Meeting, 1898.

The immediate separation of cuprous oxide and evolution of hydrogen, without formation of basic salt, which occurs at the commencement of the reaction, may be represented by the equation—

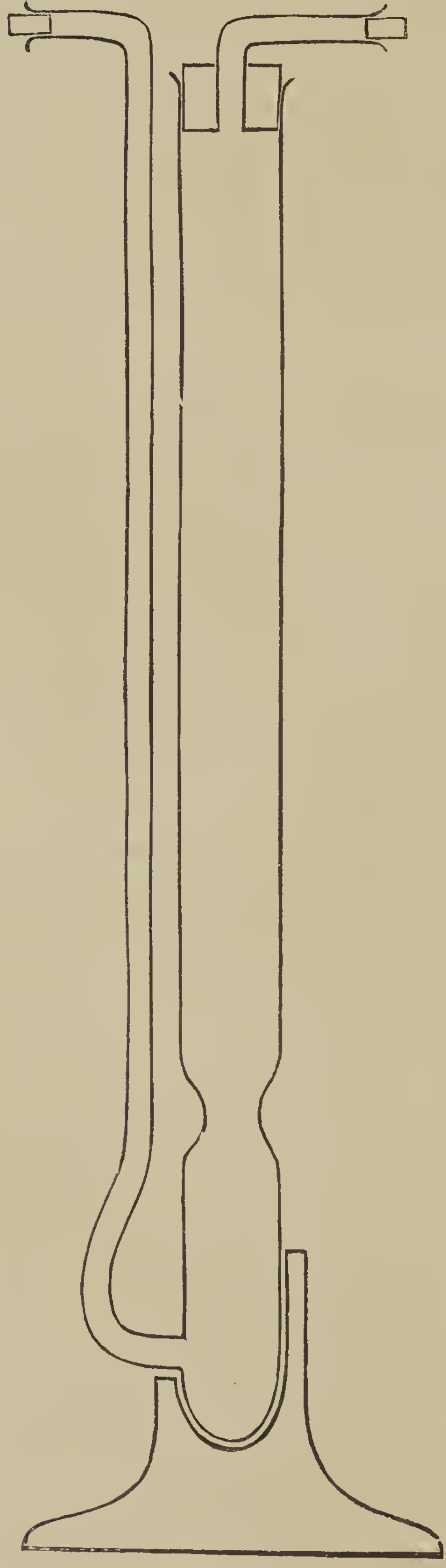
$$2Mg+2CuSO_4+H_2O=2MgSO_4+Cu_2O+H_2.$$

The action of the magnesium-copper couple has been proved to be too slow to explain the rapid escape of hydrogen, and if this were the origin of the hydrogen, its escape would not immediately follow the immersion of the magnesium.

ON A CONVENIENT FORM OF DRYING TUBE.*

By A. G. VERNON HARCOURT, F.R.S.

A common method of drying gases is to pass them through a wash-bottle containing sulphuric acid and then through a U-tube filled with fragments of pumice moistened with the same liquid. The number of corks and connections in this arrangement increase the chance of leakage. The U-tube must be supported in an upright position both when in use and afterwards, that the acid may not come in contact with the corks; if too much acid is poured in, the bend becomes blocked by a plug of liquid; there is no means of telling when the acid has become less efficient by dilution; nor is it easy to re-charge the tube with fresh acid.



The form of drying-tube shown avoids these defects. It is at once wash-bottle and drying-tube. It has one cork and stands upright; the pumice can be well drenched with sulphuric acid, the excess draining down and filling the lower part (through which the gas bubbles) to a convenient height; dilution announces itself, and the acid is easily renewed. The shape is that of a Gay-Lussac burette with a constriction about two inches from the bottom. A piece of pumice, large enough to block the constriction is first dropped in, and the tube is filled to near the top with small fragments of pumice. In charging with acid care is taken not to wet the upper part of the tube; next day the level of the acid in the lower part of the tube is marked with a strip of gummed paper. The small side tube which enters the large tube near the bottom is the inlet for gas; when the moisture absorbed has raised the level of the acid about 2 m.m. above the mark, the acid in the lower part is poured off through the small tube, and fresh acid is poured in through the pumice. The inlet and outlet tubes are made of the same height, so that a series of similar drying tubes may readily be joined together.

ON THE LUMINOSITY PRODUCED BY STRIKING SUGAR.*

By JOHN BURKE, M.A.

When two lumps of sugar are struck a flash is produced of a somewhat bluish white colour, but the light is instantaneous, and yet at the same time spreads into the sugar itself far beneath the struck surface. An almost continuous luminosity, however, has been produced by a hammer striking automatically the rim of a rapidly rotating wheel of sugar (obtained by cutting up a sugar-loaf into a number of discs); the wheels or discs being about an inch thick, so as to stand the violent hammering; the hammer, being of the nature of a pendulum about four feet in length, which was drawn aside by an electro-magnet and then let go. Curiously enough, if the impact is given when the wheel is stationary, so that only an impulse is given without rubbing, or if, on the other hand, the wheel is set spinning and the hammer is stationary and merely allowed to rub up against the wheel, the phenomenon is insignificantly small compared to that obtained when both rubbing and knocking take place together; that is, when the wheel and hammer are both working.

The spectrum of the luminosity is confined to the more refrangible end of the spectrum, commencing somewhere about F, but it is difficult to say exactly.

One difficulty in the way of observing the spectrum—and still more of photographing it—is the rapid rate at which this sugar wears out; and to overcome this the whole apparatus is fixed on rollers moved slowly along at a suitable rate to compensate for the change in the position of the sparks which would otherwise take place, and by this means the sparks or flashes of luminosity, which appear almost continuous, are made to take place always along the axis of the collimator of the spectroscope.

The fact that the less refrangible part of the spectrum is absent shows undoubtedly that the luminosity cannot be due to the particles of sugar becoming red-hot or white-hot by the impacts, but seems to show that the light produced is due either to some change in the configuration of the crystals of sugar or to some sort of chemical action

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* A Paper read before the British Association (Section B), Bristol Meeting, 1898.

* Abstract of a Paper read before the British Association (Section A), Bristol Meeting, 1898.

set up between the sugar and the surrounding air at the freshly formed surface.

To test the latter hypothesis, the spark has been produced by dropping a lump of sugar in a tall receiver, and it was found that the colour and intensity of the flash were independent of the pressure of the air—between 76 c.m. and 2 c.m. And likewise when coal-gas was substituted for air it was also found that wetting the surface of the sugar did not alter the effect; and when two lumps of sugar were struck in water, the interesting result was obtained that the light was—so far as could be judged by merely looking at it—precisely similar to that obtained in air and coal-gas.

The fact that the surrounding medium does not seem to affect either the colour or intensity of the luminosity suggests that the effect is not due to any influence of a chemical nature of the surrounding medium on the sugar, but favours the former hypothesis that the luminosity is due to the peculiar structure of the sugar itself. The experiments are being pursued further.

NEW LABORATORY GAS FURNACE.

Our illustrations show a new fireclay gas furnace manufactured by Messrs. J. J. Griffin and Sons, on lines suggested by Mr. G. T. Holloway, for use by assayers, &c., or for performing any of the furnace work required in a chemical laboratory.

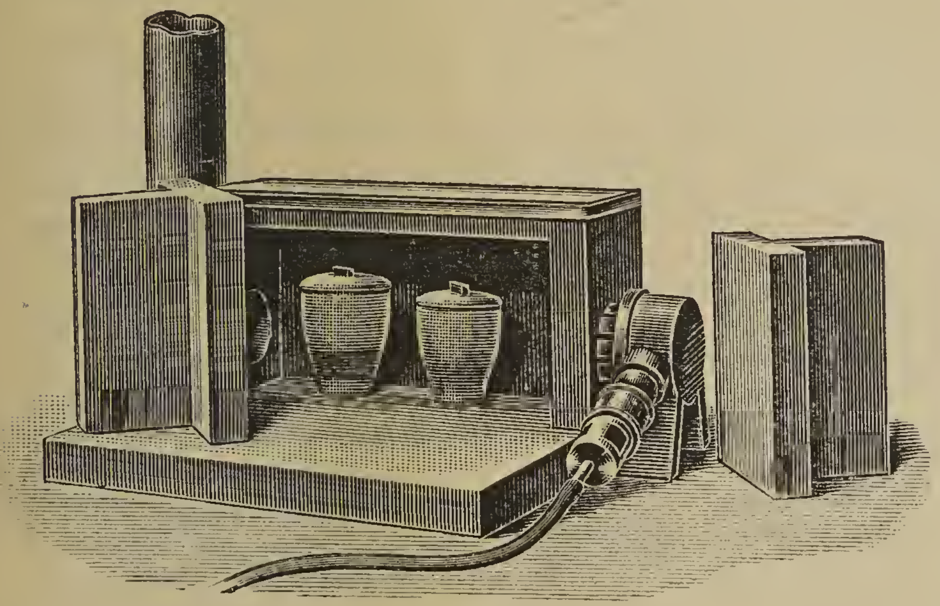

Fig. 1.

From the first illustration it will be seen that the furnace base extends forward beyond the body, and forms a convenient stand for hot crucibles, &c., and for the doors when they are drawn forward. The deep flanges on the doors serve as handles for moving them when the furnace is in use, and also support them in position and render them reversible.

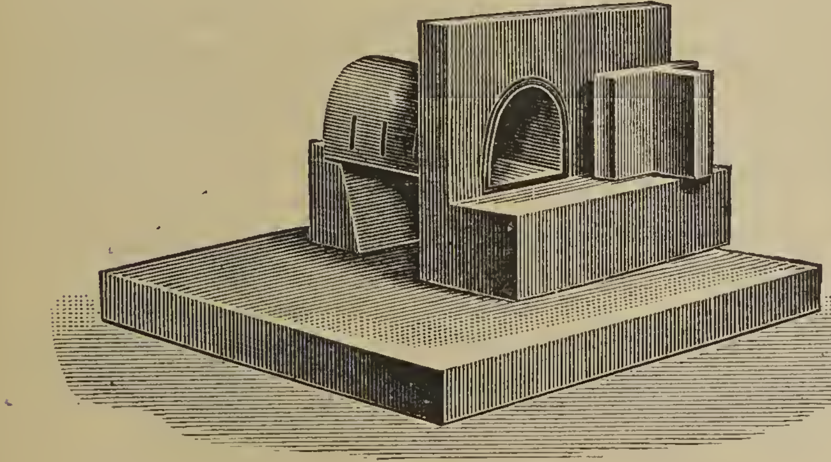

Fig. 2.

The base and body are made in independent parts, so that either may be replaced at small cost, and the base may reversed when spoiled on one side by slags, &c. This independence of body and base renders it possible to produce the furnace at a lower cost than usual and facilitates packing and transport, and it has the further advantage that the cracking which takes place with all internally-fired fire-clay furnaces is less than in those made in one piece.

For roasting, heating platinum and other small crucibles, cupelling, scorifying, and general muffle work an extra door is supplied, through which a muffle passes. The second figure shows this appliance, the body of the furnace having been removed from the base to show the arrangement more clearly, and the small door which closes the muffle aperture being shown drawn aside. The back of the muffle rests on a removable block, as shown.

This furnace, which is about 13 inches in length, is found to be suitable for all the ordinary work of a laboratory, the various improvements in its construction also greatly facilitating the work done with it.

THE PREPARATION AND PROPERTIES OF HYDRIDE OF CALCIUM.

By HENRI MOISSAN.

Preparation.—Pure crystallised calcium, prepared by the method we described in a previous communication (*Comptes Rendus*, cxxvi., p. 1753, June 20, 1898) is put into a nickel boat in a glass tube traversed by a current of pure dry hydrogen. The hydrogen is purified by being passed through two porcelain tubes at a red heat,—one filled with copper and the other with pure boron. It is then dried with fused potash and phosphoric acid, previously calcined in a current of oxygen.

At the ordinary temperature calcium does not react on hydrogen.

When the tube containing the nickel boat has been well swept by a rapid current of hydrogen, the end of the tube is sealed and the hydrogen is kept in it at a pressure of from 30 to 40 c.m. of water. The temperature of the boat containing the lime is then slowly raised, and when it reaches a dull red heat we can see it take fire in the atmosphere of hydrogen. The gas is absorbed with great rapidity, and we obtain, in place of the metal, a white substance, which is hydride of calcium.

If we perform this experiment on 1 or 2 grms. of calcium it may be done in a glass tube, but the great disengagement of heat produced by this combination may give rise to the reduction of the glass by the alkaline earthy metal, producing black spots on the glass by the setting free of small quantities of silicon.

When the reaction is carried out in nickel boats, as we have already described, it is advisable not to work on more than 5 or 6 grms. of material at a time, or else the temperature becomes too high, and we more frequently find a crystallised alloy of nickel and calcium at the line of contact with the metallic nickel.

When we wish to get a higher return of this hydride we can easily do so by putting several boats containing calcium in the tube, so that the reaction will be performed successively. The metallic tube is then placed on a gas furnace with eight jets, and by using three boats we can easily work with 15 grms. of calcium.

If the hydrogen contains nitrogen, we notice that the hydride takes a greyish yellow tint and gives off ammonia by its decomposition with water.

Properties.—Hydride of calcium is a white body, and after fusion has a crystalline fracture. Examined under the microscope it appears in thin transparent layers, some of which are again covered by very small crystals. It does not perceptibly dissociate up to a temperature of 600° *in vacuo*. Its density taken in essence of turpentine is 1·7.

In hydrogen gas we have kept hydride of calcium intact up to a temperature of the melting-point of Bohemian glass; there was neither any absorption of gas nor apparent decomposition of the hydride.

In a current of chlorine, hydride of calcium does not change to any perceptible extent in the cold; but as soon as the temperature is slightly raised, long before any sign of redness, it burns with a flame, certainly not very bright, but giving off fumes rich in hydrochloric acid. After this reaction there remains a mass having all the properties of chloride of calcium, but not containing any sub-chloride. When heated in the vapour of bromine at a dull red heat the reaction is much stronger, and the hydride decomposes with a brilliant incandescence. This same reaction occurs with iodine; a brilliant light is suddenly produced at a red heat, and at the same time there is a production of hydriodic gas.

When heated on a sheet of platinum in free air, hydride of calcium undergoes no apparent change, even at a red heat, but if heated before an oxy-hydrogen blowpipe it burns with great brilliancy, producing at the same time a flame of hydrogen. After this experiment there remains only quicklime which has been raised to its melting-point. This residue treated with water forms at first a hydrate of lime, which disintegrates forming a greyish powder, which on further treatment with water gives off hydrogen. In this strong combustion of hydride of calcium in air, a layer of lime is formed, which—on account of the heat given off by the reaction—melts, and thus covers a part of the hydride and prevents complete oxidation. When thrown into the flame of a Bunsen burner, powdered hydride of calcium gives brilliant sparks, as does lime.

In a current of pure oxygen the hydride takes fire below a red heat, and continues to burn with strong incandescence. The heat given off is so great that one can distinctly observe the fusion of the lime produced. Examined under the microscope this lime appears to be covered with small crystals. We have already shown, by our experiments with the electric furnace, with what facility lime crystallises at a high temperature.

Hydride of calcium, either in powder or in small lumps, when heated in the vapour of sulphur to a dull red heat. forms only a small quantity of sulphide, the decomposition not being complete. But if we heat a fragment of the hydride in front of the blowpipe, the reaction takes place immediately with brilliant incandescence; at the same time an abundance of sulphuretted hydrogen is given off.

At the temperature of the melting-point of glass, hydride of calcium does not react on the vapour of selenium. When heated under a glass cover filled with nitrogen, hydride of calcium undergoes no change, even when the experiment lasts two hours. After cooling the volume of gas has not altered, and a sensitive litmus-paper gives no appreciable indication of ammonia. Thus, at a dull red heat nitrogen is without action on this hydride.

On the other hand, hydride of calcium is decomposed by the vapour of phosphorus at about 500°. Hydrogen is given off, and a substance of a deep chocolate colour remains, which reacts with cold water, giving phosphuretted hydrogen.

At a temperature of 700° boron has no action on hydride of calcium. When heated to from 700° to 800° in a crucible brasqued with previously baked charcoal, hydride of calcium is partially decomposed, and carbide of calcium, giving acetylene gas on contact with water, is formed. Under similar conditions silicon and boron gave no results.

Fluoride of potassium, first melted and then powdered, was mixed with powdered hydride of calcium; this mixture heated in a test-tube gave no active result until a temperature of 500° was reached, when the hydride reacted and gave off hydrogen and vapour of potassium, Fluoride of sodium gave the same reaction.

Fluoride of silver, when ground in the cold with this hydride, became incandescent, and deflagration was produced by the admixture of powdered fluoride of calcium and metallic silver. The fluorides of lead and zinc are reduced with incandescence below 400°.

Chloride of sodium, reduced to a fine powder and mixed with hydride of calcium, undergoes at a red heat a regular decomposition, giving off vapour of sodium, which condenses, forming a metallic mirror on the cooler part of the apparatus.

Melted iodide of potassium is not attacked by hydride of calcium, while iodide of silver, when warmed, reacts with a considerable disengagement of heat.

Oxidising agents, such as chlorate or bichromate of potassium when melted, or powdered permanganate of potassium, are reduced with incandescence. The chlorates, bromates, and iodates form veritable explosives with this hydride. With perchlorate of potassium the explosion takes place in the cold, by the simple grinding of the two substances in an agate mortar. If a few m.grms. of the hydride are mixed with an excess of perchlorate of potassium, the explosion is sufficiently violent to smash the tube to pieces.

Sulphuretted hydrogen does not react below a red heat, but at a higher temperature sulphide of calcium and hydrogen are formed.

If we heat powdered hydride of calcium in an atmosphere of binoxide of nitrogen, before a red heat is reached, a lively incandescence is produced and ammonia is given off very freely.

Carbonic acid is reduced at a red heat by hydride of calcium, with strong incandescence, carbon and carbide of calcium being formed.

Warm concentrated sulphuric acid is reduced by hydride of calcium.

Fuming nitric acid has practically no action. On the other hand, these same acids when diluted with water have a vigorous action; a salt of lime is produced, and hydrogen is given off. Concentrated or dilute hydrochloric acid attacks hydride of calcium. This reaction is comparable with that which gives us hydride of copper. Anhydrous ethylic alcohol attacks it but slowly, and both benzine and essence of turpentine, when quite free from water, have no reaction in the cold. The alcoholic chlorides and iodides are without action at the ordinary temperature. The vapour of tetrachloride of carbon is decomposed by this hydride with incandescence, at about 400°, with the production of a deposit of carbon and a disengagement of hydrogen and hydrochloric acid.

The most curious reaction of this new compound is that which takes place with cold water; as soon as hydride of calcium comes in contact with this liquid, the latter is decomposed with violence, and both the hydrogen of the water as well as that from the hydride is given off, while hydrated oxide of calcium is formed:—

$$CaH_2 + 2H_2O = Ca(OH)_2 + H_6.$$

Analysis.—To determine the composition of the hydride of calcium, we made the following experiment:— A given weight of pure crystallised calcium is placed in a small tared glass tube full of hydrogen. The exact weight of the metal is taken, and then it is transformed into hydride.

Weight of calcium	0·3595 grms.
Weight of hydride	0·3760 "
Hydrogen absorbed ..	0·0165 "

which corresponds to the following centesimal composition:—

		Theory for CaH_2.
Calcium	95·61	95·23
Hydrogen	4·39	4·76

The 0·376 grm. of hydride of calcium is placed in a large gas measurer filled with mercury; into the upper part of the apparatus a few c.c. of water are passed, which immediately decompose the hydride giving a volume of hydrogen of 437 c.c. (H=766 m.m. T=+20°). The purity of this hydrogen was established by a eudiometric analysis. This volume, corrected to 0° and 760 m.m. =401·00 c.c. Theoretically, if we give to hydride of calcium the formula CaH_2 it should have produced a volume of 399·80 c.c.

Two other analyses, made under the same conditions, gave us the following figures:—

	I.	II.
Calcium	95·80	95·38
Hydrogen ..	4·32	4·60

Conclusions.—To sum up, we obtain by the direct union of calcium and of hydrogen, a transparent crystalline hydride, with the formula CaH_2. The hydride is stable at a high temperature, and is an energetic reducing agent. By its violent decomposition when in contact with cold water it strongly resembles the definite crystallised carbide of calcium we prepared in the electric. In this compound the hydrogen is comparable to the metalloids (carbon or phosphorus) and not to the metals. Even the appearance of this hydride completely distinguishes it from the hydrides of MM. Troost and Hautefeuille and the hydrogenised palladium of Graham. In reality there are two series of hydrides, some in which the hydrogen seems to be in solution in the metals, and the others forming at a more or less elevated temperature and presenting all the characteristics of definite chemical compounds.—*Comptes Rendus*, vol. cxxvii., No. 1.

SOME PRINCIPLES AND METHODS OF ANALYSIS APPLIED TO SILICATE ROCKS.*

By W. F. HILLEBRAND.

(Continued from p. 145).

Chlorine.

To make sure of getting all the chlorine, it is best to fuse with chlorine-free sodium-potassium carbonate, or even sodium carbonate alone, first over the full burner, then for a moment or two over the blast, leach with water, acidify with nitric acid, and precipitate by silver nitrate. If 1 grm. of material has been used no precipitation of silica need be feared on acidifying or on standing.

In many cases it is quite sufficient to attack the powder by hydrofluoric acid and a little nitric acid, with occasional stirring, and, after filtering through a large platinum cone, to throw down the chlorine by silver nitrate. The presence of nitric acid is necessary, since otherwise ferrous fluoride reduces silver nitrate with deposition of crystallised silver. When coagulated by heating and stirring, the precipitate is collected on the platinum cone, washed, dissolved by a little ammonia, and re-precipitated by nitric acid, when it can be collected in a Gooch crucible and weighed, or, if very small in quantity, on a small paper filter, which is then dried, wound up in a tared platinum wire, and carefully ignited. The increased weight of the wire is due to the metallic silver of the chloride which has alloyed with it.

Fluorine.

Fluorine can only be estimated by the method of Rose, care being taken to use sodium-potassium carbonate as a flux, and to avoid use of the blast if possible. The use of ammonium nitrate or chloride instead of carbonate for throwing out the silica and alumina is not to be recommended, because of loss of fluorine on evaporation (Rose). If the rocks are very basic, it may happen that the amount of silica in the alkaline solution is so small that ammonium carbonate may be dispensed with and the ammoniacal zinc oxide solution added at once.

By whatever modification of the method the silica may have been separated, the alkaline carbonate must be converted into nitrate and not chloride if phosphorus or chromium, or both, are present. To remove the chromium and the last of the phosphorus, silver nitrate in excess is added to the solution containing still enough alkaline carbonate to cause a copious precipitate of silver carbonate, in order to take up the acid set free, and thus ensure a neutral solution and consequent complete precipitation of phosphorus and chromium. After heating and filtering, the excess of silver is to be removed by sodium or potassium chloride, and sodium carbonate is to be added, when the fluorine is ready to be thrown out by calcium chloride in excess. At this stage there must be no ammoniacal salts in solution, otherwise calcium fluoride may be held in solution.

The well-washed and gently ignited calcium fluoride finally obtained in the course of this method should be converted to sulphate as a check upon its purity, and at the same time as a qualitative test to ascertain if it really is calcium fluoride by the characteristic odour of its gas. Should fluorine be found, and the weight of sulphate not correspond to that of the fluoride, the former should be dissolved in hot nitric acid and tested for phosphorus by ammonium molybdate solution. If phosphate is absent the impurity may have been silica or calcium silicate—which of these it would be difficult to decide. In the former case the fluorine might be safely deduced from that of the sulphate, but not in the latter. If the rock were rich in sulphur it might happen that calcium sulphate would be thrown down with the fluoride, but this should be removed by thorough washing. If not, and it were certainly the only impurity present, the fluorine could be calculated, after conversion of the fluoride into sulphate, by the formula—

$$CaSO_4 - CaF_2 : 2F :: \text{diff. between impure } CaSO_4 \text{ and } CaF_2 : x.$$

It is an exceptional case when there is exact agreement between the weight of fluoride and sulphate, and with the small amounts usually met in rocks the error may be an appreciable one in percentage of fluorine, though of no great significance otherwise.

There is no qualitative test which will reveal with certainty the presence of fluorine in rocks. Heating the powder before the blowpipe with sodium metaphosphate on a piece of curved platinum foil inserted into one end of a glass tube, or in a bulb tube, is not to be relied on in all cases. While as little as one-tenth of 1 per cent of fluorine can sometimes be thus detected with ease, much larger amounts in another class of rocks may fail to show.

(To be continued).

NOTICES OF BOOKS.

The Extra Pharmacopœia. Revised in accordance with the "British Pharmacopœia," 1898. By WILLIAM MARTINDALE, F.L.S., F.C.S. Serotherapy, Organotherapy, Medical References, and a Therapeutic Index, by W. WYNNE WESTCOTT, M.B. (Lond.). Ninth Edition. London: H. K. Lewis. 1898. Pp. 686.

IT is about three years since the last edition of this valuable little work was published. Naturally there are many changes and additions to be found in this, the ninth edition. Medical and chemical science never stands still, but marches steadily onwards. Notwithstanding this fact, conservative views prevailed in the revision of "The British Pharmacopœia," but the newer unofficial remedies will be found in the volume now before us, with numerous details and references as to their use. There is a small list of errata which should not be overlooked, but taking it altogether the author is certainly to be congratulated in bringing out the present edition of a book so useful

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* From the *Bulletin of the United States Geological Survey*, No. 148, p. 15, 1897.

to doctors and pharmaceutical chemists, and thus indirectly to the public at large.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Zeitschrift für Anorganische Chemie, Vol. xv.

Supersaturation: its Dependence on Crystalline Form.—M. Nicol.—The author endeavours to prove the law that when, under certain conditions of experiment, two allotropic modifications of the substance dissolved or melted may exist, the phenomenon of supersaturation or of superfusion is possible. The word allotropic should here be taken in its widest meaning, including not only amorphous and crystalline forms of the same substance, but also the crystalline modifications which may result from the union of that substance with other free molecules, such as water of crystallisation. The author has experimented on many and various substances, among which are hyposulphite of soda, borax, acetate of lead, nitrates of potassium, ammonium, and silver, acetanilide, hydroquinone, acetamide, tartaric and nitric acids, &c.

On the Constitution of Inorganic Compounds.—A. Werner.—The compounds which are formed by Anderson's reaction form the subject-matter of this paper. This name is given to the transformation undergone by the chloroplatinates of a certain number of the organic bases by which they lose successively one and then two molecules of hydrochloric acid. The author shows that such compounds are formed on the model of the ammoniacal compounds of platinum.

On the Valence of Glucinum.—A. Rosenheim and P. Woge.—The authors support the bivalence of glucinum, because it forms with the binoxalates compounds whose preparation and properties they describe, and which are ordinary double salts, while under the same conditions the tri-valent metals give complex compounds which are not double salts. On the contrary, glucinum, like the bivalent metals, forms with the bi-tartrates complex compounds which are not double salts. The trivalent metals do not form the complex compounds. Glucina does not act in the same manner as Al_2O_3, Cr_2O_3, and Fe_2O_3 with the para-molybdates, but with solutions of the alkaline bisulphites it gives crystallised double salts, as do most of the bivalent metals. The molecular weight of chloride of glucinum, by the ebullition method, using pyridine as solvent, gives a number corresponding to the formula $GlCl_2$.

On the Compounds of Platinum and Tellurium.—M. Rœssler.—Certain crystallised compounds having the composition $PtTe_2$ and PtTe are described. The first was obtained by melting platinum with an excess of finely divided tellurium, then removing the excess of tellurium by means of a concentrated solution of potash. When melted under suitable conditions this compound loses an atom of tellurium, and on solidifying forms crystals consisting of PtTe. The author suspects, but has not yet proved, the existence of a third compound, Pt_2Te.

The Hydrates of Platino-cyanide of Magnesium and their Solubilities.—MM. Hellmuth, Baron Buxhœvden, and Tammrann.—If crystals of platinocyanide of magnesium are gradually heated in a saturated solution from 0° to 100° we note that the crystals change first from red to yellow, then to a bright greenish colour, and finally become white; these colourations correspond to four different hydrates, containing respectively 6·9 to 6·6 H_2O, 5 H_2O, 4 H_2O, and 2 H_2O. The conditions under which these phenomena occur are minutely described, and curves of solubilities have been made.

MISCELLANEOUS.

Charterhouse (William Rogers' Memorial) Science and Art Schools and Literary Institute.—The Winter Session of this, one of the largest Science and Art Schools of the United Kingdom, will commence on Saturday, September 24th. During the late Session upwards of 700 students, mostly elementary teachers, availed themselves of the privileges afforded by this Institute. Instruction of a decidedly practical character is given in most of the sciences at a nominal fee; whilst in Art, at an equally low rate, students may be advanced in their studies. Classes will be held to prepare candidates for Matriculation (Lond.), the Clerical, Medical (including Mental), Legal, and other Exams. Students who aim at becoming proficient in Chemistry (Organic and Inorganic) have the opportunity of working in a well fitted laboratory. Aspirants for University Honours can, at a small expense, be assisted in their studies. Special opportunities for the study of Hygiene will be afforded this Session to Laundry and Cookery students who desire to be prepared for the examinations held by the London School Board and by the London County Council. Full particulars of the classes may be obtained from Mr. C. Smith. Those interested in education will rejoice to learn that the work commenced by the late Rev. William Rogers, M.A., and continued by a late Vice-Chairman of the London School Board, is so vigorously continued by the present President, the Rev. Henry Swann, M.A.

On the Essence of Mandarins.—J. Flatau and H. Labbé.—The authors have found 98 per cent of limonene in this essence, identical with that found in essence of Portugal, a trace of citral, and about 1 per cent of the same ether insoluble in alcohol were also present.—*Bull. Soc. Chim. de Paris.*

THE CHEMICAL NEWS.

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ADDRESS TO THE MATHEMATICAL AND PHYSICAL SECTION OF THE BRITISH ASSOCIATION.

Bristol, 1898.

By Professor W. E. AYRTON, F.R.S.,
President of the Section.

(Concluded from p. 154).

Coming now to physics proper, there is one branch which, although of deep interest, has hitherto been much neglected. We possess three senses which enable us to detect the presence of things at a distance—viz., seeing, hearing, and smelling. The first two are highly cultivated in man, and, probably for that reason, the laws of the propagation of the disturbances which affect the eyes and the ears have been the subject of much investigation, whereas, although to many animals the sense of smell is of far greater importance than those of seeing or hearing, and although, even in the human brain, a whole segment—a small one in modern man, it is true—is devoted to the olfactory fibres, the laws of the production and propagation of smell have received practically no attention from the physicist. For some time past it has, therefore, seemed to me to be of theoretical and practical importance to examine more fully into the physics of smell. Various other occupations have hitherto prevented my advancing much beyond the threshold of the subject, but, as it seems to me to open up what is practically a new field of inquiry for the physicist, I take this opportunity of putting on record some facts that have been already elucidated.

Various odoriferous substances have been employed in the experiments, and for several of these I am indebted to Mr. W. J. Pope. Although the physicist has been allowing the mechanical side of the subject to lie dormant, the chemist, I find, has been analysing flowers and other bodies used in the manufacture of scents, and then synthetically preparing the odoriferous constituents. In this way, Mr. Pope informs me, there has been added to the list of manufactured articles, during the past seven years or so, vanilin, heliotropin, artificial musk, irone, and ionone, which give the perfume of the violet; citral, that of lemongrass; coumarin, that of hay, and various others; and specimens of several of these artificial scents, together with other strongly-smelling substances, he has kindly furnished me with.

If it be a proof of civilisation to retain but a remnant of a sense which is so keen in many types of dogs, then I may pride myself on having reached a very high state of civilisation. But with the present investigation in view, this pride has been of a very empty character, since I have been compelled to reject my own nose as quite lacking the sensitiveness that should characterise a philosophical measuring instrument. The ladies of my family, on the contrary, possess a nasal quickness which formerly seemed to me to be rather of the nature of a defect, since, at any rate in towns, there are so many more disagreeable odours than attractive ones. But on the present occasion their power of detecting slight smells, and the repugnance which they show in the case of so many of them, have stood me in good stead, and made it possible to put before you the following modest contribution to the subject.

There is a generally accepted idea that metals have smells, since if you take up a piece of metal at random or a coin out of your pocket, a smell can generally be detected. But I find that, as commercial aluminium, brass, bronze, copper, German-silver, gold, iron, silver, phosphor-bronze, steel, tin, and zinc are more and more carefully cleaned, they become more and more alike in emitting *no* smell, and, indeed, when they are *very clean* it seems impossible with the nose, even if it be a good one, to distinguish any one of these metals from the rest, or even to detect its presence. Brass, iron, and steel are the last to lose their characteristic odour with cleaning, and for some time I was not sure whether the last two could be rendered absolutely odourless, in consequence of the difficulty of placing them close to the nose without breathing on them, which, as explained later on, evolves the characteristic "copper" and "iron" smell. But experiment shows that, when very considerable care is taken both in the cleaning and the smelling, no odour can be detected even with iron or steel.

Contrary, then, to what is usually believed, metals appear to have no smell *per se*. Why, then, do several of them generally possess smells? The answer is simple; for I find that handling a piece of metal is one of the most efficient ways of causing it to acquire its characteristic smell, so that the mere fact of lifting up a piece of brass or iron to smell it may cause it to apparently acquire a metallic odour, even if it had none before. This experiment may be easily tried thus:—Clean a penny *very carefully* until all sense of odour is gone; then hold it in the hand for a few seconds, and it will smell—of copper, as we usually say. Leave it for a short time on a clean piece of paper, and it will be found that the metallic smell has entirely disappeared, or, at any rate, is not as strong as the smell of the paper on which it rests. The smell produced by the contact of the hand with the bronze will be marked if the closed hand containing it be only opened sufficiently for the nose to be inserted, and it can be still further increased by rubbing the coin between the fingers.

All the metals enumerated above, with the exception of gold and silver, can be made to produce a smell when thus treated, but the smells evolved by the various metals are quite different. Aluminium, tin, and zinc, I find, smell much the same when rubbed with the fingers, the odour, however, being quite different from that produced by brass, bronze, copper, German-silver, and phosphor-bronze, which all give the characteristic "copper" smell. Iron and steel give the strong "iron" smell, which, again, is quite different from that evolved by the other metals. In making these experiments it is important to carefully wash the hands after touching each metal to free them from the odour of that metal. It is also necessary to wait for a short time on each occasion after drying the hands, since it is not until they become again moist with perspiration that they are operative in bringing out the so-called smell of metals.

That the hands, when comparatively dry, do not bring out the smell of metals is in itself a disproof of the current idea that metals acquire a smell when slightly warmed. And this I have further tested by heating up specimens of all the above-mentioned metals to 120° Fahrenheit, in the sun, and finding that they acquire no smell when quite clean and untouched with the hands.

Again, dealing with the copper group, or with aluminium, *no* smell is produced by rubbing any one of them with dry table-salt, strong brine, or with wet salt, provided that a piece of linen is used as the rubber; but if the finger be substituted for the linen to rub on brine, a smell is observed with copper and German-silver, this smell, however, being rather like that of soda; and whether dry salt, brine, or wet salt be rubbed on aluminium, a smell is noticed if the finger be used as the rubber, this smell being very marked in the case of the brine or wet salt. Again, although even when linen soaked in brine, or having wet salt on it, is used to rub tin, iron, or steel, a faint smell is noticed; this is much increased when the finger is substituted for the piece of linen.

As a further illustration of the part played by the skin in causing metallic smells, it may be mentioned that the explanation of certain entirely contradictory results, which were obtained in the early part of the investigation, when linen soaked in strong brine was rubbed on aluminium, was ultimately traced to one layer of moist linen of the thickness of a pocket-handkerchief, allowing the finger to act through it, so that an odour was sometimes noticed on rubbing aluminium with the piece of linen soaked in brine. For it was found that when two or more layers of the same linen soaked in the same brine were employed to separate the finger from the aluminium during the rubbing, no smell could be detected.

From the preceding it seems that the smell in these cases is evolved partly by contact with the finger, partly by the action of the solution of salt, and partly by the rubbing of the solid particles of salt against the metals. That the friction of solid particles against metals is operative in evolving smells is also illustrated by the smell noticed when iron is filed, or when aluminium, iron, or steel is cleaned with glass-paper or emery-paper in the air. Indeed, the smell thus evolved by aluminium Mrs. Ayrton finds particularly offensive. A slight smell is also noticed if iron or steel be rubbed in the air with even a clean piece of dry linen, and each specimen of the copper group, with the exception of the phosphor-bronze, which was tried in this way, gave rise to a faint, rather agreeable smell. No indication of odour could, however, be thus produced with aluminium or zinc when both the metals and the linen rubber were quite clean. It should, however, be borne in mind that all these experiments, where very slight smells are noticed, and especially when the odour rapidly disappears on the cessation of the operation that produced it, are attended with a certain amount of doubt, for the linen rubber cannot be freed from the characteristic smell of "clean linen," no matter how carefully it may be washed.

Before, then, a metal can evolve a smell, chemical action must apparently take place, for rubbing the metal probably frees metallic particles, and facilitates the chemical action to which I shall refer. All chemical actions, however, in which metals take part do not produce smell; for example, no smell but that of soda, or of sugar, respectively, can be detected on rubbing any single one of the series of metals that I have enumerated with a lump of wet soda, or a lump of wet sugar, although chemical action certainly takes place. Again, no metallic smell is observable when dilute nitric acid is rubbed on copper, German-silver, phosphor-bronze, tin, or zinc, although the chemical action is very marked in the case of some of these metals. Weak vinegar or a weak solution of ammonia are also equally inoperative. On the other hand, merely breathing on brass, copper, iron, steel, or zinc, which has been rendered practically odourless by cleaning, produces a very distinct smell, while a very thin film of water placed on iron or steel evolves a still stronger odour. Such a film, however, produces but little effect with any of the metals except these two, and if the whole series is lightly touched in succession with the tongue, the iron and steel smell as strongly as when breathed on, the German-silver still more strongly than when breathed on or covered with a water film, and the other metals hardly at all.

Now, as regards the explanation of these metallic smells, which have hitherto been attributed to the metals themselves. This, I think, may be found in the odours produced when the metals are rubbed with linen soaked in dilute sulphuric acid. For here, apart from any contact of the metal with the skin, the aluminium, tin, and zinc are found to smell alike; the copper group also smell alike, and the iron and steel give rise to the characteristic "iron" smell, which, in this case, can be detected some feet away. Now, it is known that when hydrogen is evolved by the action of sulphuric acid on iron, the gas has a very unpleasant smell, and this, Dr. Tilden tells me, is due to the presence of hydrocarbons, and especially of paraffin. I have been, therefore, led to think that the smell of iron or steel when held in the hand is really due to the hydrocarbons to which this operation gives rise; and it is probable that no metallic particles, even in the form of vapour, reach the nose or even leave the metal. Hence, although smell may not, like sound, be propagated by vibration, it seems probable that particles of the metal with which we have been accustomed to associate the particular smell may no more come into contact with the olfactory nerves than a sounding musical instrument strikes against the drum of the ear.

And the same sort of result may occur when a metal is rubbed, for, although in that case particles may very likely be detached, it seems possible that the function of these metallic particles may be to act on the moisture of the air, and liberate hydrogen similarly contaminated; and that in this case also it is the impurities which produce the smell, and not the particles of the metal with which we have been accustomed to associate it.

This view I put forward tentatively, and to further elucidate the matter I am about to begin a series of smell tests in various gases, artificially dried, with metals as pure as can be obtained.

I next come to the diffusion of smell. From the experience we have of the considerable distance at which a good nose can detect a smell, and the quickness with which the opening of a bottle of scent, for example, can be detected at a distance, I imagined that tubes not less than 15 or 20 feet in length would be required for ascertaining, even roughly, the velocity at which a smell travels. But experiment soon showed that when the space through which a smell had to pass was screened from draughts, it diffused with surprising slowness, and that feet could be replaced by inches in deciding on the lengths of the tubes to be used. These are made of glass, which is relatively easy to free from remanent smells.

When the room and tube had been freed from smell by strong currents of air blown through them, the tube was corked up at one end and taken outside to have another cork, to which was attached some odoriferous substance, inserted at the other end. The tube was now brought back to the odourless room, and placed in a fixed horizontal or vertical position, and the unscented stopper was withdrawn. As a rule, immediately after the removal of the stopper, a smell was observed, which had been transmitted very quickly through the tube by the act of corking up the other end with the stopper carrying the odoriferous material. This first whiff, however, lasted only a very short time, and then a long period elapsed before any further smell could be detected at the free end of the tube, whether that end was left open or closed between times. Finally, however, after, for example, about eighteen minutes in the case of a 3-foot horizontal tube, having a large cotton-wool sponge saturated with oil of limes attached to one cork, the smell became definite and recognisable.

It would, therefore, appear that the passage of smell is generally far more due to the actual motion of the air containing it than to the diffusion of the odoriferous substance through the air. And, as a striking illustration of this, the following is interesting:—After the stopper had been in contact with the odoriferous substance for some time, it, of course, acquired a smell itself, which gradually spread in the room in which the experiment was made. And although this smell was due simply to the exposed part of the stopper, while the air inside the tube was at one end in contact with a mass of the odoriferous substance itself, the only place where the smell could *not* be detected during the course of the experiment was the space inside the open end of the glass tube. And, what seemed very surprising, it was found necessary, in several cases, to blow air through the room to clear out the smell which emanated from the *outside* of the stopper before the smell coming along the tube from the mass of odoriferous substance which was *inside* it at the other end could be detected. A further proof of the important part played by the motion of the air in diffusing smell was the fact that a strong smell at the free end of the tube could at any time be caused by merely loosening the stopper to which the scented sponge was attached; for sniffing at the free end then made a draught through the tube which brought the scent with it.

Further, although the glass tubes were coated outside with a thick layer of non-heat-conducting material, so as to check the formation of convection currents, due to difference in the inside and outside temperature, caused by handling, the rate of travel of a smell from a given odoriferous material was found to be much quicker when the tube was vertical than when it was horizontal. But this, I am inclined to think, may have been caused by a small convection current which still was produced in spite of these precautions.

For, as suggested by Dr. Ramsay several years ago, a substance must have a molecular weight at least fifteen times that of hydrogen to produce a sensation of smell at all, and, further, since camphor—with which many of my experiments have been made—has, when vaporised, a density about five times that of the air, it seems unlikely that scent vapour should diffuse much more quickly upwards through a vertical column of air than through a horizontal one. At the same time, not only are the tests with the glass tubes very striking, but the general impression which exists that smells rise,—indeed the very fact that the nasal channels of animals open downwards, tends to show that, whether due to draughts or not, smells have really a tendency to ascend. And the following result obtained with glass tubes closed at one end with stoppers carrying respectively camphor, menthol, oil of limes, &c., and at the other end with corks, is instructive on this point. For, on uncorking such a tube after it had been closed for a long time and allowing the odour to stream out of it through the open air towards the experimenter's face, it was always found that the tube had to be brought much closer when the scent stream was poured downwards than when she was in a vertical position and it was allowed to ascend, although, when it was poured downwards, the experimenter brought her nose into as favourable a position as possible for receiving the smell, by lying down with her head thrown well back.

As an illustration of the inefficiency of diffusion alone to convey a smell, you will find that if you hold your breath, without in any way closing your nose either externally or by contracting the nasal muscles, you will experience no smelling sensation even when the nose is held close to pepper or a strong solution of ammonia, or even when camphor on a minute tube is introduced high up into the nostril. Mere diffusion from the lower nasal cavity into the upper cannot apparently take place with sufficient ease to produce the sense of smell, so that an actual stream of air through the upper portion of the nose seems necessary even when the nose is a very sensitive one. This stream, for substances placed outside the nose, is produced by breathing *in*, no smell being detected while breathing *out*. On the other hand, if a substance be placed inside the mouth its flavour is recognised when the air is forced outwards through the nostrils—that is, at each expiration. Hence we may experience alternately two totally different smells by placing one substance outside the nose and the other in the mouth, the one smell being noticed in inhaling and the other in exhaling. And the latter can be increased by smacking the lips, which, I think, has really for its object the forcing of more air through the nostrils at each expiration.

Experiments on the propagation of smells in a vacuum have also been commenced in my laboratory, and the results are no less surprising than those obtained with the propagation in air. A U-tube, 7 inches high, had the odoriferous substance placed inside it at the top of one limb, and a very good vacuum could be made by allowing mercury to flow out of the tube. Then the two limbs were separated by raising the mercury column, and air being admitted at the top of the other limb, without its coming into contact with the odoriferous substance, the nose was applied at the top of this limb.

When liquids like ammoniated lavender, smelling salts, solution of musk, and amyl acetate were employed, and various devices were used for introducing the liquid, and preventing its splashing when it boiled on exhausting the air, it was found that the time that it was necessary to leave the two limbs connected for a smell to be just observable was reduced from a few minutes or seconds when the tube was filled with air to less than half a second for a good vacuum; with solid camphor it was reduced from twenty minutes to one second, and when moist rose leaves were used from fifty minutes to two seconds. But with solid particles of musk the time was not reduced below twenty minutes by taking away the air, while with dried lavender flowers and dried woodruff leaves no smell could be detected after the two limbs had been connected for many hours, and a good vacuum maintained, These experiments are, of course, somewhat complicated by variations in the amount of odorous surface exposed, but they seem to indicate that with these particular dried substances either the rate of evolution of the scent or its rate of propagation, or both, are very slow even in a good vacuum.

I have also carried out some tests on the power of different substances to absorb various scents from the air. Lard, it is well known, is used to absorb the perfume from flowers in the commercial manufacture of scents, perhaps because it has little odour of its own, and because the scent can be easily distilled from it. But if lard, wool, linen, blotting-paper, silk, &c., be shut up for some hours in a box at equal distances from jasmine flowers, dried woodruff leaves, or from a solution of ammonia, I find that it is not the lard, but the blotting-paper, that smells most strongly when the articles are removed from the box. On the other hand, when solid natural musk is employed, it is the wool that alone acquires much smell, even after the box has been shut up for days.

Another noteworthy fact is the comparatively rapid rate at which grains of natural musk are found to lose their fragrance when exposed to the air. The popular statement, therefore, that a grain of musk will scent a room for years supplies but another example of the contrast between text-book information and laboratory experience.

The power of a smell to cling to a substance seems to depend neither on the intensity of the smell nor on the ease with which it travels through a closed space. Musk has but a faint smell, but the recollection of the greeting of a rich Oriental survives many washings of the hands. The smell of rose leaves, again, is but faint, and it travels very slowly through air in a tube; and yet the experiments on its propagation in the glass vacuum apparatus were rendered extremely troublesome, by the difficulty experienced in removing the traces of the smell from the glass between the successive tests. Rubbing its surface was quite ineffectual, and even the mercury had to be occasionally shaken up with alcohol to free it from the remanent smell. In fact we found, as Moore put it,—

> "You may break, you may shatter the vase if you will,
> But the scent of the roses will cling to it still."

This absorption of scents by glass, and the ease with which I found that jasmine flowers could be distinguished from woodruff leaves, even when each was enclosed in a series of three envelopes specially prepared from glazed paper, and when many precautions were taken to prevent an odour being given to any of the envelopes in the operation of closing, as well as to prevent its diffusion through the joins in the paper, led me to try whether an actual transpiration through glass could be detected with the nose. For this object a number of extremely thin glass bulbs were blown from soda and from lead glass, so thin that they exhibited colours like a soap-bubble, and felt, when gently touched, like very thin oiled silk; and after a little ammoniated lavender, amyl nitrite, ethyl sulphide, mercaptan, solution of musk, oil of peppermint, and propylamine had been introduced into them respectively, they were hermetically sealed, and placed separately in glass stoppered bottles.

In some cases, on removing the stopper from a bottle after many hours, a faint odour could be detected, but so, generally, could a minute flaw after much searching; the crack, however, being so slight that it did not allow sufficient passage of the air to prevent the bulb subsequently breaking, presumably from changes of atmospheric pressure. And in those cases where a smell was detected without any flaw being found in the glass, the subsequent breaking of the bulb put an end to further testing. The question, therefore, remains unanswered.

In presenting this brief introduction to the physics of smell, I have aimed at indicating the vast territory that waits to be explored. That it will be found to contain mines of theoretical wealth there can be no doubt; while it is probable that a luxuriant growth of technical application would spring up later on. Already, for example, Mrs. Ayrton unintentionally picks out inferior glass by the repugnance she shows at drinking water out of certain cheap tumblers. To conclude, I may say that one of my fondest hopes is that an inquiry into the physics of smell may add another to the list of wide regions of knowledge opened up by the theoretical physicist in his search for answers to the questions of the technical man.

ON THE COOLING CURVES OF FATTY ACIDS.*

By **A. P. LAURIE** and **E. H. STRANGE**.

The melting-points of mixtures of fatty acids were determined by Heintz, and the tables are quoted in the text-books. They show that the mixtures have a lower melting-point than either of their constituents, thus showing a close analogy to the behaviour of many alloys. We therefore determined to apply to these bodies a method of investigation similar to that used by Professor Roberts-Austen in his experiments on alloys.

The melted fatty acids are placed in a test-tube surrounded by melting ice, and a thermal junction connected to a mirror galvanometer inserted. The results are photographed on a moving plate. The plate is calibrated by means of a second thermal junction attached to a thermometer, and immersed in a large volume of water. The cooling curves obtained in this way are of considerable interest. The fatty acids investigated have been palmitic, stearic, lauric, and myristic acids. The cooling curve of a pure fatty acid turns sharply round when the solidifying point is reached, runs straight up the plate till the solidifying is finished, and then turns sharply off again. One per cent of another fatty acid quite perceptibly alters the shape of the curve, so that the character of a cooling curve seems a good test of purity. When a larger portion of a fatty acid is introduced a second latent heat-point is developed, the curve showing a discontinuity below the solidifying point of the mixture. As the solidifying point is lowered by introducing more and more of the second fatty acid, this discontinuity is gradually merged in the common melting-point of the mixture, thus reproducing the phenomena observed by Professor Roberts-Austen in the case of certain alloys. The question, therefore, of the true cause of this discontinuity is opened up, as we can hardly suppose that two homologous acids are forming compounds. We are now repeating our experiments with synthetically prepared organic bodies of known constitution, and studying also the cooling curve of water.

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* A Paper read before the British Association (Section B), Bristol Meeting, 1898.

THE CARBOHYDRATES OF THE CEREAL STRAWS.*

The work, which was carried out in the agricultural season of 1897, has been reported upon in a paper published in the *Journal of the Chemical Society*, 1898, p. 459. The purpose of these later investigations was to trace the effect of removing the seed-bearing organs upon the carbohydrates of the stem. The results were, however, negative, adding another confirmation to the conclusion previously arrived at, that the carbohydrates of the stem tissues are built up with a constant ratio of "furfural-yielding" to normal hexose carbohydrates. Further evidence was also obtained that these two groups of carbohydrates are in the earlier stages of growth similarly attacked by boiling dilute acids, and after such hydrolysis are similarly fermented by yeast.

It must in fact be admitted that as condensation to furfural is by no means an exclusive characteristic of C_5 carbohydrates, there is no evidence whatever that the furfuroids of the barley straw are, in the early stages of growth, pentose-anhydrides or pentosanes.

There now appears in the *Journ. Fed. Inst. Brewing*, 1898, p. 438, an article by Tollens under the title "On the Carbohydrates of Barley and Malt, with special reference to the Pentosanes," in which, as a result of yeast fermentations of the products of acid hydrolysis of brewers' grains, the author arrives at the following conclusions:— "From the behaviour of these furfural-yielding substances on fermentation we are forced to the view that they behave, to some extent, similarly to the ordinary hexoses, and somewhat different from the pentoses, for when brought into contact with yeast they exhibit certain manifestations of fermentation; but they give rise to the formation of but little alcohol and much acid. It must be concluded from this that the furfural-yielding substances . . . contain a certain amount of other substances more susceptible to fermentation than arabinose and xylose. They may contain glycuronic acid or oxycelluloses. . . ."

We are very glad to have this confirmation from so great an authority as Professor Tollens, and we will not quarrel with his decision "to retain the old name pentosanes for this group of substances," instead of "the indefinite name of furfuroids proposed by Cross and Bevan." We will only remark that, as the idea has been abandoned that they are exclusively and definitely pentosanes, it appears more logical to adopt a term of corresponding significance.

We ourselves have recently carried out a more extended series of fermentation experiments which further define these products, and the results of this work will be published in the course of the autumn.

Generally, the position for which we have long contended may be taken as fully established, viz., that the plant world affords a group of furfural-yielding bodies, probably carbohydrates, which are susceptible of fermentation by yeast.

We have next resumed the study of the problem of the relationship of such compounds to the normal hexoses, on the basis of the purely chemical probabilities. We have previously shown that furfuroids are produced from the hexoses by many processes of oxidation. One such process, which we had overlooked, appeared from the researches of Fenton in the province of the dicarboxylic acids to be capable of extension to other hydroxy-compounds, such as the carbohydrates—that is, the action of hydrogen peroxide in presence of iron salts. A research in this direction has led to positive results. We have not only succeeded in producing furfuroids in some quantity —7 to 9 per cent of the hexaldoses—but we find that di-

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* Third Report of the Committee, consisting of Professor R. Warington (Chairman), Mr. Manning Prentice, and Mr. C. F. Cross (Secretary). (Drawn up by Mr. Cross). Read before the British Association (Section B), Bristol Meeting, 1898.

carbonyl derivatives are produced reacting with phenylhydrazin acetate in the cold to form dihydrazones, which appear to be osazones. We have published a preliminary account of this research in the *Journal of the Chemical Society*, 1898, p. 463, and since the publication of the paper we have been joined in the investigations by Dr. R. S. Morrell, of Cambridge University. Results have been obtained confirming and extending those of our preliminary paper, and these will be published in the course of the autumn. We have every expectation that the investigations will lead to results of physiological significance by elucidating processes actually taking place in the plant cell.

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending August 31st, 1898.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To Major-General A. De Courcy Scott, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, September 10th, 1898.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Aug. 1st to Aug. 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined by us all were clear, bright, and well filtered.

The deficiency of rain still continues. The fall at Oxford during this month has been 1·64 inches; this fell on eight days. The average for the last thirty years is 2·32 inches, leaving a deficiency of 0·68 inch. The total deficiency for the year is now 6·17 inches, or 38 per cent.

Our bacteriological examinations of 255 samples have given the results recorded in the following table; we have also examined 36 other samples, from special wells, standpipes, &c., making a total of 291 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	690
New River, filtered (mean of 25 samples) ..	70
Thames, unfiltered (mean of 26 samples) ..	2620
Thames water, from the clear water wells of five Thames-derived supplies (mean of 126 samples)	28
Ditto ditto .. .. highest	493
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 26 samples) ..	1958
River Lea, from the East London Company's clear water well (mean of 26 samples) . ..	51

The excellent quality of the water supplied to London during the past month has been thoroughly maintained.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

A NEW DEPARTURE IN THE MANUFACTURE OF SALTS OF THE HIGHER OXIDES.

By H. N. WARREN, Principal, Liverpool Research Laboratory.

Unfortunately, so far, no satisfactory method for the manufacture of the above-mentioned compounds has been introduced, save that of fusion of the said oxide in contact with alkali bases. This method, besides being tedious, is at the same time most destructive upon the plant employed, which naturally accounts in a large measure for the still high market rate of these compounds.

True, a partial improvement in the method of fusion was introduced by the author some years previously, by the introduction of suitable quantities of alkaline borates in proportion to the melt. This, besides effecting a more complete union at a much lower temperature, also effects a considerable saving of the plant in use; whilst, at the same time, the lowering of the temperature naturally prevents to a large extent volatilisation of the alkalis.

In order, therefore, to surmount as much as possible the former obstacles, several electrolytic processes have of late been protected, each differing from the other with a sufficiency to admit of the inventor securing a further protection only, either as regards electrolytes employed, or, on the other hand, the choice of suitable diaphragms has been discussed. Bearing these facts in mind, the author is about to establish a more direct process, which, with due precautions, it is hoped will evolve a more theoretical yield than any of the processes now in use.

A general and condensed outline of the new process is as follows:—It consists of the conversion of such alloys as spiegeleisen, ferromanganese, chromeisen, &c., by the direct contact of aqueous solutions of the alkalis aided by electric energy, into their corresponding salts, such as chromates, manganates, &c. The baths for the conversion of these alloys have so far been constructed of glass and partially covered with graphite plates, which constitute the negative electrolyte, while to the positive is attached the alloy in question. The solution or solvent employed, consisting for the most part of caustic alkali of a definite gravity to which has been added a small percentage of other oxidants which have been found to aid in the conversion, which takes place rapidly under a pressure of 8 volts, with the formation of manganates or permanganates, as desired (ferrates may, if desired, be thus obtained, or a corresponding oxide precipitated), or by slight alteration of the process a solution of chromate may be obtained.

Liverpool Research Laboratory,
18, Albion Street, Everton, Liverpool.

ON SELENITE OF COPPER AND ITS USE IN THE PREPARATION OF SELENIC ACID.

By R. METZNER.

I. *Preparation of Seleniate of Copper.*

Selenium was transformed into a solution of selenious acid; this was oxidised by means of a current of chlorine. The reaction which takes place is the following:—

$$SeO_2 + 2Cl + H_2O = 2HCl + SeO_3.$$

It is exothermic, and gives off about +30 cals.

It is as well not to operate on a too concentrated solution; the proportion present should not exceed 10 per cent, if we wish to get a complete oxidation. When the liquid has taken a yellow tint and gives off a strong odour of chlorine, we prove on a small sample that there is no more selenious acid present. We then proceed with the neutralisation of the mixture of the selenic and hydrochloric acids by means of pure oxide of copper made by the calcination of the nitrate: this dissolves rapidly, giving a solution at first green, but becoming blue when the neutralisation is almost complete. We then add oxide of copper precipitated from the nitrate and perfectly washed with warm water, and which is further boiled to diminish its volume. This oxide dissolves much more rapidly than the calcined oxide, and by its use we can easily neutralise the selenic acid. The solution obtained, mixed with chloride and seleniate of copper, is partially evaporated down; on cooling it deposits beautiful prisms of seleniate of copper, which are carefully dried, and purified by further crystallisations effected by allowing the hot saturated solutions to cool; this salt is, as we shall see later on, much more soluble hot than cold. Further, chloride of copper being deliquescent, the concentration of the mixture of the seleniate and the chloride can be pushed very far, and, the former being insoluble in a saturated solution of the latter, we obtain a complete separation.

The chlorine I used was from an iron reservoir containing the gas in the liquid state; thus I experienced no difficulty in preparing several kilogrms. of seleniate of copper.

It is certain that it would be more easy to effect the operation of the selenious acid with bromine, and I tried the operation under the same conditions of dilution as with the chlorine. The reaction which might take place is the following one:—

$$SeO_2+2Br+H_2O=2HBr+SeO_3.$$

It also gives off 10·4 cals.; but the oxidation which is partially produced when we pour bromine water into a solution of selenious acid is never complete, and, if we add the theoretical quantity of bromine necessary to oxidise a determined quantity of selenious acid, the liquor remains coloured by bromine, while at the same time unoxidised selenious acid remains.

II. *Properties of Seleniate of Copper.*

Solubility.—This varies greatly with the temperature. I have found in 1 litre of a saturated solution:—

At 15°	257 grms. of seleniate.
At 35°	346 ,, ,,
At 55°	435 ,, ,,

At a higher temperature towards 70° a saturated solution of seleniate of copper decomposes, as has been shown by Mitscherlich (*Ann. de Chim. et de Phys.*, Series 2, vol. xxxvii.), depositing a green crystalline matter which he could not analyse, but which corresponds to the formula $2(CuOSeO_3),CuO,5H_2O$, as is shown by the following analysis:—

	Found.			
	I.	II.	Mean.	Calculated.
Copper ..	31·0	29·9	30·45	31·1
Selenium..	27·0	26·8	26·9	26·7

The deposit is the more abundant as the liquor contains more seleniate, so that in order to obtain a notable quantity it is necessary to commence with a solution saturated at 50°. Seen through the microscope this substance appears to consist of small clinorhombic prisms, transparent, pale green, and unmodified. They are but slightly affected by cold water, which enables them to be washed to get rid of the mother-liquor.

Selenide of copper dissolves, especially when warmed, in selenic acid, diluted with three or four times its volume of water. On cooling, the solution leaves a deposit of pale blue striated prisms, in which I have found copper 20·6, selenium 27·0, and which have therefore the same composition as the original crystals.

When the amount of selenic acid is augmented, the above blue crystals become transformed into a granular white matter, which under the microscope—even with a low power—appear to be formed of transparent tabular crystals. They correspond to the formula $CuO,SeO_3,2H_2O$. When submitted to the action of dry air, the crystals of seleniate of copper lose water. At 100° only one molecule remains, and the crystals then correspond to the formula CuO,SeO_3,H_2O.

Heat of Formation.—This has been measured by precipitating a normal solution of seleniate of copper by an equivalent quantity of potash in the calorimeter. I thus found—

$$SeO_4Cu+2KOH=SeO_4K_2+CuO\text{ ppt.}+H_2O= \\ =+13{\cdot}06\text{ cals.},$$

from which it is deduced that—

$$SeO_3\text{ dis. }+CuO\text{ ppt.}=SeO_4Cu\text{ dis. . . . }+18{\cdot}12\text{ cals}$$

Heat of Solution.—We found for this—

$$SeO_3,CuO,5H_2O+\text{water}=SeO_4Cu\text{ dis. . . . }-2{\cdot}66\text{ cals.}$$

III. *Electrolysis.*

Pure seleniate of copper was obtained, as has been described above, but more especially free from hydrochloric acid; I effected its electrolysis warm, by operating on saturated solutions.

The apparatus, which is very simple, is composed of two large platinum crucibles; one of them, the larger, was placed at the bottom of a very wide porcelain crucible holding the solution; the other, smaller one, was suspended a short distance from the first one by means of platinum wires. These two crucibles were connected with the poles of a dynamo, and the whole arranged so that the lower crucible should be entirely submerged, while the upper one was only partially so; by putting in mercury as ballast it could be made to sink to any desired distance from the lower one. Finally, a current of air kept the liquid thoroughly mixed so that the electrolysis was regular. With a current of two to three volts and five ampères the copper is deposited in the form of a light spongy mass, which falls into the lower crucible: in ten hours we obtained 300 c.c. of dilute monohydrated selenic acid, in 2 to 3 litres of water.

I have always carefully watched for the disappearance of the last traces of copper, so as not to keep the current on longer than the time necessary for complete separation, and to prevent the possible phenomena of reduction. I thus obtained a very pure selenic acid; I am especially certain that it contained neither copper, chlorine, nor selenious acid.—*Comptes Rendus*, cxxvii., No. 1.

ON THE ESTIMATION OF PHOSPHORIC ACID.

By H. LASNE.

In an article by Léo Vignon which recently appeared in the *Comptes Rendus* (vol. cxxvi., p. 1522), he pointed out the divergences obtained by the separate precipitation of the solutions of a superphosphate treated first with water, then with citrate of ammonia, or by previously mixing the two solutions. The total of the two first figures, he says, will always be less than the third, and that to a considerable degree. A result of this kind would be such as to throw doubt on the exactitude of the estimation of phosphoric acid by precipitation in presence of citrate of ammonia; while according to my experience I do not believe there is a more exact estimation, or one less subject to uncertainties, while at the same time it is thoroughly practicable. Every day in my laboratory we make a large number of estimations of phosphoric acid in superphosphates, often separating the results, and nothing of this kind has ever been observed.

We here give some experiments made since the publication of Léo Vignon's article, with a view to confirm in a special manner the observations we have just made.

I. Mineral superphosphate obtained from a phosphate from the Somme.
II. Superphosphate from degelatinised bones.
III. Superphosphate from green bones.

	Weight of pyrophosphate.		
	I. Grm.	II. Grm.	III. Grm.
On 1 grm. of superphosphate soluble in water	0·2622	0·1186	0·1320
Insoluble in water, but soluble in citrate	0·0089	0·1369	0·0400
Total	0·2711	0·2555	0·1720
On the two solutions united ..	0·2715	0·2570	0·1732

The differences, it will be seen, hardly amount to a m.grm.,—that is to say, they come within the range of errors of observation; the experiments were purposely carried out under the same conditions as used in ordinary practice, and without any special precautions. The precipitations are always done in the evening, and the filtering takes place the following morning, after standing fifteen or sixteen hours. I have, however, shown (*Bull. Soc. Chim.*, Series 3, xvii., p. 823) that the precipitation is complete after three or four hours' standing or fifteen minutes' agitation, but that, under these conditions, there remains in the precipitate a small quantity of trimagnesic phosphate which disappears completely after sixteen hours' contact in presence of citrate of ammonia.

I have also shown (*loc. cit.*) that the precipitation is integral—that it is not influenced by substances which generally accompany phosphoric acid, except silica and fluorspar, which should be previously removed. But it fortunately happens that neither silica nor fluorspar enter into solutions with the superphosphates, otherwise the estimation would be complicated.

To sum up, the ammonio-magnesic phosphate is *completely* insoluble in a solution containing one-third of its volume of ammonia at 22°.

In order to confirm my previous results I made the following experiment with the greatest care, with the object of finding out whether very small quantities of phosphoric acid could be precipitated in the state of ammonio-magnesic phosphate:—

I. 3·5 grms. of phosphate of ammonia were dissolved in 100 c.c.
II. With 10 c.c. of No. I. I made 100 c.c.
III. With 10 c.c. of No. II. I made 100 c.c.
IV. With 10 c.c. of No. III. I made 100 c.c.

10 c.c. of each of these solutions were taken, and precipitated in the usual manner; that is to say:—
40 c.c. of water (to bring it up to the usual volume).
25 c.c. of citrate of ammonia at 400 grms. of citric acid per litre.
60 c.c. of ammonia at 22°.
20 c.c. of ammoniacal chloride of magnesia at 20 grms. of magnesia per litre.

If we add the wash waters of the precipitate we get a total volume of about 200 c.c. After calcining to form pyrophosphate I obtained the following weights:—

I.	II.	III.	IV.
0·3159	0·0317	0·0034	0·0003

That is in phosphoric acid:—

0·2121	0·0203	0·0021	0·0002

With an approximation which was entirely satisfactory I obtained down to the lowest figure the following proportion:—

1000 : 100 : 10 : 1.

I attach the greatest importance to Experiment No. IV. The beaker in which the precipitation took place, after having been emptied and drained, showed slight signs of losing its polish, caused by the crystals of the ammonio-magnesic phosphate. After weighing, the precipitate was re-dissolved, and the presence of phosphoric acid proved by means of nitro-molybdate of ammonium. From this it results that 1 m.grm. of phosphoric acid per litre is *integrally* precipitated in the state of ammonio-magnesic phosphate. There is therefore no reason to fear that the precipitation of very poor solutions is incomplete. If it does not immediately show in a distinct manner, it is sufficient to leave the solution, after agitation, from the evening to the next morning, for the whole of the phosphoric acid to be precipitated.

SOME PRINCIPLES AND METHODS OF ANALYSIS APPLIED TO SILICATE ROCKS.*

By W. F. HILLEBRAND.

(Concluded from p. 159).

Sulphur.

If present in the form of soluble sulphates, simple boiling with hydrochloric acid suffices, which should be done in an atmosphere of carbonic acid if pyrite or other oxidisable sulphides are present.

The sulphur of sulphides, chiefly pyritic, may sometimes be determined by extraction with aqua regia or potassium chlorate and hydrochloric acid, but not always; so that it is better by far to fuse with sulphur-free sodium carbonate and a little nitre over the Bunsen burner and for a few moments over the blast, fitting the crucible into a hole in asbestos board to prevent access of sulphur from the flame. The aqueous solution, after filtration, is just acidified by hydrochloric acid, and the sulphur at once thrown down at boiling heat by barium chloride, without fear of separation of silica in a bulk of about 250 c.c. when 1 grm. is operated on. It is well that this is so, for evaporation on the water-bath heated by gas to remove silica would in many cases involve an error fully equal to the sulphur present by contamination from the sulphur of the gas burned.

Owing to the small amount of sulphur in rocks, special purification of the barium sulphate obtained is hardly ever needful, especially as it has been precipitated in absence of iron. Should there be fear of a trace of silica being present, it can be removed by a drop of hydrofluoric and sulphuric acids before weighing the barium sulphate.

This, of course, gives the total sulphur in the rock. If soluble sulphates and sulphides as well as insoluble sulphates and sulphides are present together, the sulphur of the first is found in solution after extraction by hydrochloric acid in a carbon dioxide atmosphere, and that of the decomposable sulphides by collecting the hydrogen sulphide evolved. In the residue the sulphur of the insoluble sulphides can be estimated, or from the total sulphur found in another portion its amount can be calculated. The error involved in the above estimation of the sulphur of soluble sulphides, due to the possible reducing effect of hydrogen sulphide on ferric salts, is probably negligible. Most of the hydrogen sulphide would be expelled before any such action could take place and probably before the ferric salts were largely attacked, but of course the small proportion of sulphur set free as such from pyrrhotite would escape estimation and introduce further uncertainty. In general, it would be safe enough to assume the composition Fe_7S_8 for pyrrhotite. However carefully all these separate determinations may be carried out, the final figures for ferrous and ferric oxides can hardly be regarded as more than approximations when much sulphide is present.

Boron.

To the best of the writer's belief it has never been necessary in this laboratory to estimate boron in a silicate rock. Should it become necessary to do so, since most silico-borates are insoluble minerals, it would probably be necessary to fuse with sodium carbonate, extract with

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* From the *Bulletin of the United States Geological Survey*, No. 148, p. 15, 1897.

water, and apply the method of Dr. Gooch (*Proc. Amer. Acad. Arts Sci.*, 1886, p. 167; *Bull. U.S. Geol. Survey*, No. 42, p. 64, 1887; Chemical News, vol. lv., p. 7, 1887), depending on expelling the boron as methyl borate by repeated distillations with methyl alcohol in nitric or acetic acid solutions, and binding the boric acid by a known weight of lime, the gain in weight being B_2O_3. Fluorine would have to be first removed by calcium nitrate or acetate before freeing the boron.

(For a useful improvement in the way of collecting the boric ether in ammonia before bringing in contact with the lime, &c., see Penfield and Sperry, *Am. Journ. Sci.*, 3rd Series, vol. xxxiv., p. 222, 1887; also Moissan, *Comptes Rendus*, vol. cxvi., p. 1087, 1893, and *Bull. Soc. Chimique*, vol. xii., p. 955, 1894, who modifies the Gooch distilling apparatus and insures complete condensation of the boron in the distillate).

Nitrogen.

Nitrogen has been found in igneous rocks, or the minerals occurring in them, by several observers. Thus, H. Rose ("Quantitative Analyse," Finkener edition, p. 673) says that pitchstone gives off ammoniacal water on heating; Silvestri (*Gazz. Chim. Ital.*, v., p. 303, 1875) mentions a nitride of iron in lavas from Etna; Sandberger finds ammonium carbonate to be given off from certain rocks of Pribram; the writer has shown nitrogen to exist in uraninite; Ramsay and others have noted it in traces with or without helium, &c., in numerous minerals; and lately Erdmann (*Ber. Deutsch. Chem. Gesell.*, xxix, p. 1710, 1896) has found it to be given off as ammonia on treating various minerals of "ancient igneous rocks" with a caustic alkali. Leudeking also found ammonium sulphate in a barite from Missouri, the presence of which the writer was able to confirm.

During the last two years it has been noted in this laboratory on three separate occasions, when analysing as many different series of ores, roofing-slates, and eruptive rocks, that ammonia, either in the form of chloride or sulphate or even as free ammonia, was given off on heating. Its appearance was not limited to one or a few specimens of a series, but seemed to be characteristic of all, and to be afforded by the unbroken rock as well as by the powdered sample. Not knowing the precise conditions under which the specimens were collected, it is impossible to affirm positively that the ammonia may not have been due to recent organic contamination of some sort, especially in the case of the slates, but it is believed that a more critical collection of material will not alter the general result. Its amount was sometimes readily determinable by Nesslerisation, being as high as 0·04 per cent in some slates. Carbonaceous organic matter was absent from most of these, but doubtless existed in them in their early history. In their case the ammonia was, in part at least, evolved as such, imparting a strong alkaline reaction to the water in the upper part of the tube. The presence of sulphides, fluorides, or chlorides in the rock might cause the ammonia to appear as a sublimate of sulphate, fluoride, or chloride. Speculation on this matter would be altogether premature, but attention is now called to it in the hope that other observers may be led to look for and investigate similar appearances. It should be borne in mind that the nitrogen present would not necessarily appear as ammonia or ammonium salts, since it might be given off in the elemental condition, as with the gases obtained from uraninite.

Special Operations.

The problem often presents itself of ascertaining the composition of that portion of a rock powder which is soluble in special reagents or in a reagent of a particular concentration. No precise directions can be formulated to meet such cases. The procedure must vary with the character of the constituents of the rock and with the object which it is sought to attain, and only in exceptional cases can a separation of this kind be sharp. Much depends on the degree of fineness of the powder and on the length of time it is exposed to the action of the reagent.

Detection of Nepheline in presence of Olivine.—For confirmation of the microscopic diagnosis, Prof. L. V. Pirsson (*Am. Journ. Sci.*, 4th Series, vol. ii., p. 142, 1896) has indicated a means of detecting nepheline in presence of olivine, as in nepheline basalts, based on the very ready solubility of nepheline, as compared with olivine, when boiled for but one minute with a sufficiency of very dilute nitric acid (1 : 40). Gelatinisation of the filtrate on evaporation is taken as evidence of the presence of nepheline. If olivine is present in quantity, however, this test must not be accepted at once as final, for some, if not all, olivines are much more soluble in nitric acid of the above strength than Professor Pirsson was led to believe from his original tests. If, therefore, on evaporation of the filtrate, much iron is indicated, the gelatinisation may well be due to olivine alone or in part, and then the quantitative relation of silica to iron plus magnesium should be ascertained. It must also be borne in mind that any other very soluble silicates present will be more or less affected, and that apatite is largely or wholly dissolved. It is possible that still more dilute nitric, or perhaps some other, acid may exert a slighter solvent action on olivine without being appreciably less effective in dissolving nepheline, &c. In combination with a quantitative analysis of the extract the method is, perhaps, susceptible of a wider application than the particular case for which it was first used. It is well worth further study.

Estimation of Soluble Silica.—Very often in treatment by acids silica is separated in gelatinous or granular form mixed with the unattacked minerals, and it becomes necessary to remove or estimate this silica, or else to discriminate between soluble and insoluble silica already existing together. Usually a boiling solution of sodium carbonate has been employed for this purpose. Its action is frequently slow and incomplete, and the extraction must often be repeated many times as to silica, and its solvent action on other minerals is often marked. The filtering of hot saturated solutions of the carbonate is also unpleasant. Hence the substitution of a caustic hydroxide, as KOH or NaOH, has been advocated, especially by Michaelis (*Chemiker Zeitung*, 1895, xix., p. 1422), who maintains with force that quartz is absolutely unattacked by boiling 10 per cent solutions (10 per cent Na_2O), or even by 25 per cent solutions when digested on the water-bath, and that different results are probably due to the mechanical carrying off in the filtrate of portions of the fine powder, which is notoriously difficult to filter. In the case of separated silica the hydroxides certainly give very good results. Solution is almost immediate and complete in a quite dilute liquid, and the difficulty met with in filtering may often be overcome by faintly acidifying. If the dilution is sufficient, no separation of silica results from so doing, and less difficulty is experienced in filtering and washing, especially if very dilute acid is used for the latter.

Estimation of Minute Traces of certain Constituents.

If, as sometimes may happen, the problem is presented of examining rocks for traces of gold, silver, and other elements which are not ordinarily looked for, as in Sandberger's investigations bearing on the origin of the metalliferous contents of veins, large weights of material must be taken, up to 50 grms. or more. This involves the use also of large quantities of reagents, the purity of which must then be looked to with the utmost care. Special directions to meet such cases cannot now be given, nor even a complete reference list of the scanty and scattered literature on this subject. Sandberger's own writings deal but little with its analytical side, and from its inaccessibility in the Washington libraries the writer is as yet unacquainted with the report by Von Foullon "Ueber den Gang und die Ausführung der Chemischen Untersuchung" ("Jahrbuch der Bergakademie, Leoben u. Pribram," 1887, p. 363), following Sandberger's own paper in the general report "Untersuchungen der Nebengesteine der Pribramer Gänge" (see Note). The present writer has published a few data as to gold, silver, lead, zinc, &c. (*Mon. U.S. Geol. Survey*, vol. xii., 1886, Appendix B, pp. 592-596), in Mr. F. S. Emmons's report on "The Geology and Mining Industry of Leadville"; and Mr. J. S. Curtis (*Mon. U.S. Geol. Survey*, vol. vii., 1884, pp. 120-138), in his report on "The Silver-Lead Deposits of Eureka, Nevada," has given his method of assaying rocks for traces of gold and silver.

Note.—From Sandberger's report it appears that the rocks were treated successively with water, acetic acid, boiling dilute hydrochloric acid for two days, and finally hydrofluoric acid; the several extracts and final residue of fluorides (and pyrite) being separately examined for heavy metals. The products of distillation were also examined. A striking fact observed in all cases was the complete insolubility of the pyrite, even after the severe treatment mentioned. This speaks strongly in favour of the correctness of ferrous iron estimations in silicates by the hydrofluoric and sulphuric acid method when pyrite is present unaccompanied by other sulphides. (See p. 107).

Preliminary Qualitative Analysis.

A complete qualitative analysis of a rock, preceding the quantitative examination is in most cases a sheer waste of time. A few constituents may now and then be specially looked for, but in general time is saved by assuming the presence of most of them and proceeding on that assumption in the quantitative analysis.

Summation of Analytical Results.

As is well known, a complete silicate rock analysis which foots up less than 100 per cent is generally less satisfactory than one which shows a summation somewhat in excess of 100. This is due to several causes. Nearly all reagents, however carefully purified, still contain, or extract from the vessels used, traces of impurities, which are eventually weighed in part with the constituents of the rock. The dust entering an analysis from first to last is very considerable, washings of precipitates may be incomplete, and if large filters are used for small precipitates the former may easily be insufficiently washed.

Given the purest obtainable reagents, an ample supply of platinum, facilities for working, and a reasonably clean laboratory, there is no excuse for failure on the part of a competent chemist to reach a summation within the limits 99·75 and 100·50. Failure to attain 100 per cent in several of a series of analyses of similar nature should be the strongest evidence that something has been overlooked. Excess above 100·5 per cent should be good ground for repeating portions of the analysis in order to ascertain where the error lies, for it is not proper to assume that the excess is distributed over all determined constituents. It is quite as likely, in fact more than likely, to affect a single determination, and one which may be of importance in a critical study of the rock from the petrographic side.

Quality of Reagents.

It is due to say that all analyses performed in the Survey laboratories have been made with the purest reagents obtainable, either by purchase in the open market or by special preparation on the part of manufacturers or in the laboratory. The best acids made in this country are of a high grade, and need no re-distillation except for special experiments. Ammonia has always been redistilled at short intervals; and no sodium carbonate which exceeds 2½ m.grms. of total impurity in 20 grms. (0·012 per cent) is used for the main portions, in which silica, alumina, &c., are to be estimated. For other portions, as phosphoric acid, fluorine, sulphur, a poorer grade is entirely allowable, provided it is free from the element to be determined, and from any other which might interfere with its estimation.

Hydrofluoric acid was always freshly distilled with potassium permanganate until the introduction of ceresine bottles afforded an article sufficiently pure for all but the most exacting work. Care must be exercised even yet, however, that no particles of paraffin or ceresine are floating on the acid, and that the latter is free from traces of chlorine whenever hydrofluoric acid is to be used for bringing the chlorine into solution.

Potassium bisulphate has usually been prepared in the laboratory from sulphuric acid and potassium sulphate, since it is not always to be bought of satisfactory quality. Even then the normal sulphate had first to be examined, for it has been found to contain on different occasions, notable amounts of lead, calcium, and silica.

The phosphorus salt used for precipitating magnesium has been found to contain iron, and calcium is sometimes a constituent of ammonium oxalate. The latter has therefore to be purified or specially prepared, as also oxalic acid, ammonium chloride (in which latter manganese has been observed), and occasionally other reagents. Some hydrogen peroxide contains fluorine, which renders it unfit for use as a chemical reagent.

A "C.P." label is no guarantee whatever of the purity of a reagent; hence no chemicals should be taken on trust because of bearing such a label. Every new purchase should be examined, if it is one in which purity is a desideratum. In general all so-called "C.P." chemicals should at least stand the tests laid down by Krauch ("Die Prüfung der Chemischen Reagentien," 3rd ed., Berlin, Julius Springer, 1896). Of late, the firm of E. Merck, in Darmstadt, has begun to advertise preparations of a certain guaranteed purity, thus inaugurating a long-needed reform in this direction. Even with them, however, the guarantee should be checked, at least until long experience shall have shown the precaution to be superfluous.

To his colleague, Dr. H. N. Stokes, who kindly examined the original draft of this paper, the writer is indebted for several suggestions which have been made free use of in the foregoing.

ON SOME COMPOUNDS OF TRIVALENT VANADIUM.*

By JAMES LOCKE and GASTON H. EDWARDS.

The green solution obtained when vanadic acid is reduced by nascent hydrogen has been but very slightly studied. That it contains salts of vanadium in the trivalent state was recognised by Roscoe (*Ann. Chem.* (*Liebig*), *Suppl.*, vii., 78), in the course of his elaborate investigation on the chemical nature of this element. Roscoe, however, made no attempt to study the products which could be obtained from the solution which he prepared by dissolving the anhydrous chloride, VCl_3, in water, and failed to make any comparison between that body and the chlorides of other trivalent elements.

The first compounds to be isolated from a vanadic solution were prepared by Peterson (*Journ. Prakt. Chem.* (2), xl., 44, 1889), who examined in a very thorough manner the fluoride and its double salts with the fluorides of other metals. His results pointed to a close resemblance between vanadium sesquioxide and its derivatives and the compounds of the groups formed by aluminium, chromium, manganese, and iron. Thus, the compound $K_2VF_5.H_2O$ exhibits in its general properties, solubility, &c., close similarity to the analogously constituted salts of aluminium, iron, chromium, and manganese. Ammonium vanadifluoride, $(NH_4)_3VF_6$, is isomorphous with the ferric salt, $(NH_4)_3FeF_6$, described by Marignac (*Ann. Chim. Phys.*, (3), lx., 306), and Petersen prepared other members of the series in $(NH_4)_3CrF_6$ and $(NH_4)_3AlF_6$. A similar relation was observed between double salts with

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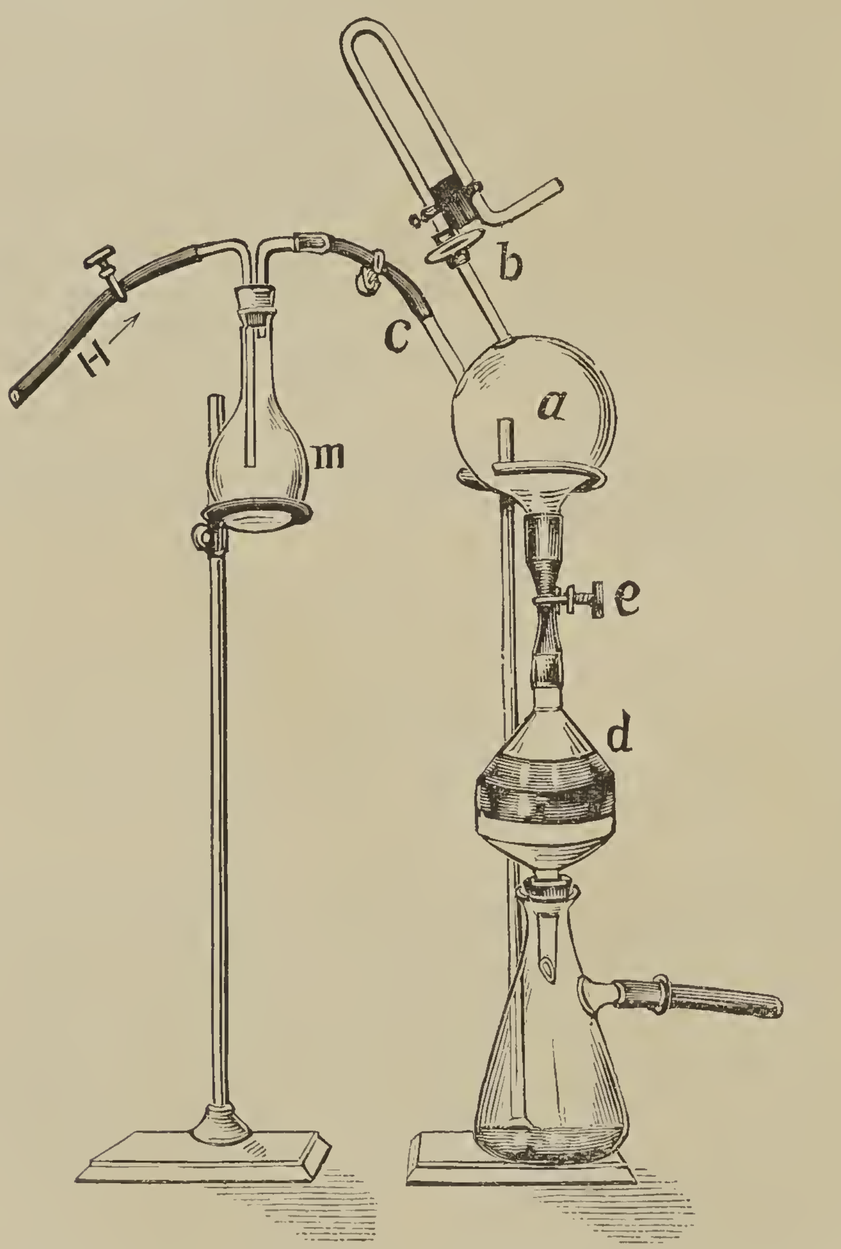
* From the *American Chemical Journal*, xx., No. 7.

the fluorides of divalent metals, such as $CoVF_5{\cdot}7H_2O$, $CoCrF_5{\cdot}7H_2O$, &c.

Petersen's work and the conclusions drawn from his results were further substantiated by the recent investigations of Piccini (*Ztschr. Anorg. Chem.*, xi., 106; xiii., 441) on the alums of vanadium. He succeeded in isolating the salts $NaV(SO_4)_2{\cdot}12H_2O$, $KV(SO_4)_2.12H_2O$, $NH_4V(SO_4)_2\ 12H_2O$, $RbV(SO_4)_2{\cdot}12H_2O$, $CsV(SO_4)_2.12H_2O$, and $TIVSO_{42}.12H_2O$, With the exception of a short article by Brierly (*Journ. Chem. Soc., London*, xlix., 822), who prepared a vanadium sulphuric acid, or "alum acid"* $V(SO_4)SO_4H.4H_2O$, the above investigations embrace practically all that has been published on vanadic salts.

We have recently undertaken the preparation of a number of other compounds, the analogues of which are of characteristic nature in the case of chromium, in the hope of ascertaining more definitely the influence which the atomic weight of vanadium exerts upon the development of the properties common to the compounds of the group: aluminium, vanadium, chromium, manganese, iron, and cobalt.



The chief difficulty which an investigation of this kind presents lies in the extreme readiness with which vanadic solutions absorb oxygen, with formation of vanadyl salts. Petersen was able to start directly from the anhydrous sesquioxide, which is soluble in hydrofluoric acid. The solutions of vanadic sulphate used by Piccini in the preparation of the alums were obtained simply by the electrolysis of vanadic acid in a solution of sulphuric acid. These methods, while satisfactory in individual cases, are of course limited in their applicability, and they could not be used in the preparation of such compounds as a vanadicyanide, sulphocyanate, or the like. We were therefore compelled to start out from the readily oxidisable vanadic hydroxide, precipitated by an alkali after the reduction of the pentoxide with sodium amalgam.

In order to protect the hydroxide and solutions from oxidation, all operations were carried out in an atmosphere of hydrogen. For this purpose the apparatus shown in the accompanying figure was employed. The pear-shaped bulb *a*, of which we had several pieces, holds about 500 c.c. Over its drawn-out end, which is two-thirds of an inch in diameter, passes a piece of thick-walled, soft-rubber tubing, which can be closed by a stop-cock *e*. The tube *b* is of capillary diameter, fitted with a glass cock, and bent over on itself, to more securely prevent the entrance of air when this cock is open. *c* is a somewhat wider tube, which serves for the introduction of reagents, and is closed by a stop-cock when necessary.

For heating on the water-bath, the bulb is placed on the latter, mouth downward, while a rapid current of hydrogen is passed in at *c*, *a* being open. The contents of the bulb may be boiled in a similar manner, the bulb then resting on its side. Reagents are added by means of a small flask *m*, fitted with a cork holding two short tubes, one of which is connected with the hydrogen generator. The reagent having been introduced into the flask (a test-tube is also convenient) the air in the latter is displaced by hydrogen, and the second tube then connected with *c*. The flask is then simply inverted, whereupon the reagent runs into the bulb.

The most important and difficult operation involved in the work was of course the filtration and washing of the vanadic hydroxide. To perform this without exposing the substance to the air, a Buchner's funnel was used, to which was joined by a wide rubber band a well-fitting piece of apparatus, *d*, like an inverted funnel. The stem of the latter was of the same diameter as the mouth of the bulb. Before attaching this filtering apparatus to the bulb, it was entirely filled, together with the suction-flask, with water, and the latter then displaced by hydrogen. Connection was then made, slight suction applied, and the stopcock at the mouth of the bulb opened. The precipitate was washed with water from which the air had been expelled by boiling, from a flask connected as for the introduction of reagents.

When the next operation involved the solution of the precipitate in an acid, the filtrate was drawn off by suction through the pump, the suction-flask rinsed with the water from one or two additional washings, and the acid then introduced as above. The solution was then transferred, either to another bulb, or, if it was to be evaporated to crystallisation, to a crystallising-dish, the side tube of the suction flask being in that case held below the surface of some benzene placed in the dish.

By taking proper care in the observance of minor details, such as the filling of the tubes with water before making connections, &c., we were able almost entirely to obviate the danger of oxidation; and after a little practice we could carry out the operations of filtration and the like almost as rapidly as in the open air. In one afternoon, starting out with vanadium pentoxide, we have prepared vanadium dihydroxide, $V(OH)_2$, washed it, redissolved in hydrochloric acid, and brought the solution into a desiccator. In spite of all the operations subsequent to the reduction of the vanadic acid, the final solution possessed the true lavender colour of vanadious salts, without a trace of green or brown. Roscoe describes such a solution as being a more sensitive reagent towards oxygen than is pyrogallol itself.

The vanadium preparations which we used in this work were placed at our disposal through the kindness of Prof. Paul Jannasch, of Heidelberg, Germany. They consisted chiefly of thoroughly purified vanadates of sodium and ammonium. These compounds were worked up as follows: Enough of the substance to yield about 5 grms. of vanadium hydroxide was dissolved in a small quantity of water, 10 c.c. of concentrated hydrochloric acid were added, and the solution boiled with alcohol to reduce the vanadic acid to vanadyl dichloride, $VOCl_2$. After the alcohol had been driven off, the solution was transferred to a bulb, and while a rapid current of hydrogen was led

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* Chromium is the only other alum-forming metal which yields such an acid, $Cr(SO_4)SO_4H$.

through the latter, 5 per cent sodium amalgam was gradually introduced in small lumps, the solution being in the meantime kept acid by the occasional addition of hydrochloric acid. The reduction was continued until the solution just began to lose the pure green colour of the vanadic salts and assume a bluish-green tint, due to compounds of the next lower degree of oxidation. The operation required the addition of about 700 grms. of amalgam.

The mercury was next drawn off, the solution filtered, transferred to another bulb, and treated in the cold with just enough ammonium hydroxide to precipitate the vanadic hydroxide[*] completely. The latter comes down as a dirty green flocculent precipitate, which absorbs oxygen with the greatest avidity. It was allowed to stand for some time, and then filtered and washed thoroughly with warm water from which the air had been expelled. From this precipitate the following salts were obtained by solution and crystallisation.

Vanadium Trichloride, $VCl_3.6H_2O$.—Halberstadt (*Ber. d. Chem. Ges.*, xv., 1619, 1882) mentions the fact that when the anhydrous chloride, VCl_3, is dissolved in water and the solution evaporated over sulphuric acid, a very unstable crystalline compound is obtained. Piccini mentions in a footnote to his first article on the vanadium alums (*Ztschr. Anorg. Chem.*, xi., 107, 1896) that he had obtained this substance in distinct crystals, and found it to have the above composition. This footnote escaped our notice when first reading his article, and at the time of preparing the compound we supposed we were the first to have isolated it. As, however, nearly three years have elapsed since his article was sent in for publication, we may be allowed to describe the compound, yielding to him the priority of its discovery.

It is obtained by dissolving vanadic hydroxide in concentrated hydrochloric acid, and evaporating the green solution to dryness in a vacuum-desiccator. The salt separates out from the syrupy liquid in large green prisms, some of which attained with us the length of nearly half a centimetre. It dissolves in water with extreme readiness, yielding, like the other neutral vanadic salts, a brown solution which becomes green on acidification. The salt is very deliquescent, and on exposure to the air for any length of time dissolves in the water absorbed, and is oxidised to vanadyl dichloride. It is readily soluble in both alcohol and ether, but no distinct crystals could be obtained from its solution in these liquids.

In the analysis of the substance the solution was acidified with nitric acid and the chlorine precipitated with silver nitrate. The vanadium was determined in another portion by titration from the tetravalent to the pentavalent state with iodine, according to Browning's method (*Ztschr. Anorg. Chem.*, i., 158). The water was estimated by difference:—

	Calculated for $VCl_3 \cdot 6H_2O$.	Found.
V	19·24	18·96
Cl	40·10	39·95
H_2O	40·66	41·09
	100·00	100·00

An attempt was made to measure the crystals, but they proved too hygroscopic. Their optical properties, however, were found to conform to the rhombic system. Salts of composition similar to that of this compound are seen in $AlCl_3 \cdot 6H_2O$, $CrCl_3 \cdot 6H_2O$, and $FeCl_3 \cdot 6H_2O$.

Potassium Vanadichloride.—An attempt was made to prepare from the chloride a double salt analogous to those of the series $R_2FeCl_5 \cdot H_2O$, in which R is K, Rb, NH_4, &c. A few grms. of the trichloride were dissolved in concentrated hydrochloric acid, the calculated quantity of potassium chloride added, and the mixture left to crystallise in a vacuum. The product consisted chiefly of green crystals of a somewhat lighter shade than that of the pure vanadium chloride, but it was impossible to isolate these completely. A vanadium determination, made in as pure a product as we could obtain, showed that it contained 22·41 per cent V. The quantity calculated for the anhydrous compound $KVCl_4$ is 22·03 per cent V.

Vanadium Bromide, $VBr_3 \cdot 6H_2O$.—This compound was prepared in a manner strictly analogous to that by which the chloride was obtained, pure concentrated hydrobromic acid being used. It crystallises with less readiness than the chloride, and decomposes more easily. In other respects the two compounds were closely similar. The bromide decomposes more or less on solution in water, leaving as a residue a small quantity of a brown substance, probably a basic bromide. Like the chloride, it is soluble in both alcohol and ether, to a green solution. The analysis was carried out as in the case of the chloride.

	Calculated for VBr_2+6H_2O.	Found.
V	12·83	12·62
Br	60·10	59·65
H_2O	27·07	27·73
	100·00	100·00

The iodide could not be obtained. Vanadium hydroxide dissolves in hydriodic acid as readily as in hydrochloric or hydrobromic, but the solution turns brown on evaporation and eventually leaves only an amorphous, brownish-black residue, only partially soluble in water.

Potassium Vanidicyanide, $K_3V(CN)_6$. — For the preparation of this compound, it was found more convenient to start out from the anhydrous vanadium trichloride, which we prepared according to the method of Halberstadt (*Ber. d. Chem. Ges.*, xv., 1619, 1882). About 5 grms. of this substance were dissolved in as little water as possible[*] and slightly acidified with hydrochloric acid. A concentrated solution of potassium cyanide containing about one and a half times the calculated quantity of the salt was placed in a bulb, and the vanadium chloride solution then added. The mixture at once assumed the form of a thick, deep purple paste, which gradually became thin again, though without at first losing its colour, and remaining almost opaque. This part of the reaction was observed by Petersen (*J. Prakt. Chem.*, xl., 50), who states that he thus obtained a dark blue solution. The blue colour, however, is in fact due only to very finely divided particles of the original precipitate suspended in the solution, which is itself of a deep wine colour. After shaking for some time the liquid cleared, and only a few flakes of a brown residue, presumably the hydroxide, remained undissolved. It is absolutely necessary to have a considerable excess of potassium cyanide present, as the precipitate dissolves with great difficulty, and a clear solution cannot otherwise be obtained.

The wine-coloured solution, after being filtered, was treated with just enough alcohol to bring about incipient precipitation, and then allowed to stand for some hours surrounded by ice-water. A fine precipitate separated out, which consisted of a mixture of potassium cyanide and vanadicyanide, and, in addition to this, comparatively large crystals of the latter collected on the sides and bottom of the vessel. These alone were saved, the rest of the product being removed by lixiviation. The crystals were repeatedly washed by decantation with 95 per cent alcohol, and finally with ether, and dried in a vacuum-desiccator.

(To be continued).

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[*] Potassium hydroxide does not work as well for this purpose, as it dissolves more or less of the vanadic hydroxide.

[*] The formation of the hydrated chloride is readily seen when a quantity of the anhydrous chloride is added to about its own volume of water. It dissolves with a hissing sound, and, on cooling, the liquid solidifies to a green crystalline mass. On addition of more water, this dissolves to a brown solution.

MISCELLANEOUS.

Deterioration of Paper.—The Report of the Committee of the Society of Arts on the Deterioration of Paper has now been published, price 1s., and can be obtained on application to the Secretary, Society of Arts, John Street, Adelphi, W.C. Two Appendixes are printed with the Report:—1. Abstracts of Papers on German Official Tests, 1885—96. 2. Précis of Correspondence.

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THE CHEMICAL NEWS.

Vol. LXXVIII., No. 2028.

STANDARDS OF PURITY FOR SEWAGE EFFLUENTS.*

By Dr. S. RIDEAL, D.Sc.(Lond.), F.I.C.

The progress made within the last few years in the bacterial processes for the treatment of sewage has drawn into question the interpretation of analytical results as well as the different standards of purity, by which effluents are to be judged to be acceptable or otherwise. At the present time some consensus of opinion is absolutely necessary.

Opinions have in many cases been founded almost solely on the permanganate process of oxidation, which has the advantage of being easy and rapid in execution, but is open to the following objections:—

1. So many modifications have been introduced in procedure, that the figures obtained by different observers are seldom comparable, as instanced in the recent discussion at Manchester.

2. It mainly measures the carbonaceous matters, which are not the most dangerous.

3. It is incomplete even in measuring these, since many of them are very resistant to permanganate if used, as ordinarily, at low temperatures. For this reason I prefer to work at a higher temperature—namely, that of a water-bath at about 80° C.

4. The interference of nitrites, which are abundant in certain stages of purification, of high chlorides, and of iron and manganese salts derived from a chemical treatment, has not been satisfactorily eliminated, even by the adoption of time limits, such as three minutes, fifteen minutes, two and a half or four hours.

In perfectly fresh human excreta, taking both solids and liquids together, the amount of nitrogen somewhat exceeds the chlorine. It is evident that the proportion between them will remain unaltered whatever volume of water be added, provided the water contains only the ordinary small amount of natural chlorine, as long as the nitrogenous matters do not undergo alteration. Therefore the factor expressing the relation between chlorine and nitrogen will be applicable to sewages generally, independent of their dilution. In subsequent changes, while the Cl will remain unaffected, the total nitrogen will suffer diminution, the loss being due to its escape in the form of gases, such as free nitrogen and nitrous oxide. The extent to which this important purification has been effected will be indicated by the above proportion, which I propose to call the "residual ratio," and prefer to express in percentages of the chlorine.

If Cl be the chlorine of the sewage,
N the total nitrogen,
R the "residual ratio,"

the formula will be—

$$R = \frac{N \times 100}{Cl}.$$

In cases of great dilution, or of an excessive amount of chlorine in the water supply, the expression will become—

$$R = \frac{N \times 100}{Cl - W};$$

W being the chlorine in the water. The simpler formula, however, is in general sufficient.

As nitrogen is significant of the more dangerous forms of pollution, a calculation of the ratio between the different forms of nitrogen furnishes more useful information than a mere consideration of its amount, inasmuch as nitrogen compounds when oxidised are harmless, but when unoxidised are liable to occasion smells, and to be in other respects deleterious. A certain quantity of nitrogen is lost as gas during the changes, but the residue will give a minimum measurement of the original sewage strength. The proportion between the oxidised and unoxidised nitrogen will then denote the extent to which the sample has been purified. A judgment can therefore be formed from the sample without an analysis of the original sewage, as the chlorine contents also give a clue to the strength, and thus such a method would have an advantage over the ordinary system of calculating sewage purification, as it obviates the difficulty of obtaining conformable samples. Even where, as I have elsewhere insisted should be done, a correction is made to a standard chlorine value in comparing the sewage entering and the effluent leaving a certain works, the system I suggest will still have great advantages.

As ammonia must be recognised as a preparatory or transition, and not a finished product, it must be considered as part of the residual unoxidised sewage, and only indicates progress towards complete purification, and gives a criterion as to whether a process is working satisfactorily. A large number of the failures in sewage disposal methods have been owing to the effort to obtain by chemical treatment or filtration a liquid from sewage which should bear some resemblance to drinking water; such an end is impossible without impracticable expenditure, time, and space, attended by disastrous breakdowns at intervals. Fortunately methods have been found which by natural agencies allow us to carry the purification to a rational and harmless stage, when such factors as time, light, volume of oxygen, and various life of a river will be more than sufficient to deal with the effluent.

A few examples to show how the percentage of oxidation reveals the purification effected by different agencies may be quoted here:—

		Parts per 100,000 of nitrogen.				
	Oxygen consumed.	As NH_3.	Organic.	Total unoxidised.	As nitrite and nitrate.	Percentage of oxidation.
A raw sewage . ..	6 66	3·0	6·12	9·12	none	none
A filtrate effluent ..	0·78	2·4	0·92	3·32	1·16	26·0
Another ditto. . ..	0·36	0·92	0·44	1·36	1·09	44·5
London river water	0·20	0·0016	0·049	0·051	0·305	86·0
Same filtered.. ..	0·176	none	0·026	0·026	0·254	91·0
Deep well in chalk .	0·013	none	0·008	0·011	0·450	97·6

Furthermore, one has to consider not only the chemical but also the pathogenic qualities, and these are ignored by all existing standards. It is obvious that a very small amount of nitrogen or carbon, if in the form of ptomaines, would be sufficient to condemn an effluent. I have noticed that many dilute putrid sewages of offensive character have shown less albumenoid or organic nitrogen than the condemnatory limits of existing standards, so that these arbitrary rules are of little or no value.

On the other hand, when a sewage has been subjected to nitrification, although the albumenoid ammonia may be higher than the old standards, the presence of nitrate seems to have a beneficial influence upon the quality of such sewage, and under these circumstances a greater quantity of albumenoid or organic nitrogen may be tolerated.

The multitude of bacteria in sewage is so enormous, and their character so various, that a mere counting of their numbers must be unmeaning and inaccurate. The ratios, however, between either those liquefying and not

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* A Paper read before the British Association (Section B), Bristol Meeting, 1898.

liquefying gelatin, or between the aërobic and non-aërobic, or between those growing at ordinary temperatures and at blood heat, give much more valuable information.

Whilst therefore any absolute number as a standard is undesirable, only a low number of organisms of the Coli group should be permissible in an effluent, with an absence of dangerous pathogenic forms.

Absolute sterility in an effluent is at present out of the question, nor in general would it be necessary or even advisable, inasmuch as subsequent organic improvement would be prevented, but the destruction of pathogenic forms could be completed by a "finisher" like chlorine when special danger was present.

Dr. Dupré some years ago introduced a method of ascertaining the condition of healthiness or otherwise of an effluent by enclosing it in a bottle and determining the free oxygen present before and after keeping. This seems a natural way of carrying out the "oxygen consumed" test. He observes (*Analyst*, August, 1898):—"Pure water remained aërated when bottled up, but water containing sewage de-aërated itself. An effluent that did not appreciably de-aërate itself might be admitted anywhere without fear of putrefaction." Unfortunately, although the actual work of this test can be carried out in a few minutes. the sample had to be allowed to stand for five to ten days.

On similar—but less natural—lines, the "Incubator Test," adopted in the Manchester report on systems of sewage purification, maintains an effluent by itself at a warm temperature (five days at 80° F.), and determines the oxygen absorbed in three minutes before and afterwards, at the same time noticing any change of odour. The result is, however, again arbitrary, as an effluent is not intended to be stored by itself, but, when finished, to be discharged at once into water which is moving and aërated.

The results seem to be more favourable to effluents which have been sterilised by a chemical or precipitation process, but which have notoriously in many cases given rise to a subsequent nuisance, than to those containing the materials, bacterial and chemical, for rapid self-purification in a river.

Mr. Dibdin has recently put forward this test, which he describes as follows:—"He had long since adopted in his own mind a physiological standard, viz., that the quality of an effluent should be such that fish could live healthily in it, . . . such a definition involves necessarily the absence of poisons and the presence of oxygen." But while an effluent which kills fish is obviously unhealthy, it does not follow that one where fish will live is therefore a good one. It is well known that fresh-water fish are gross feeders, and fish in large numbers are often seen to congregate at the mouths of sewers where fæcal matter is visibly floating, being attracted by the fragments of food and insects carried down by the sewage. Fish, in fact, are more affected by muddy water and by chemicals from factories than by excreta.

Amongst the standards which have been proposed in the past, or have been adopted by local bodies, are the following, some of which have been repeatedly quoted in papers on the subject, while others are gathered tentatively from published documents, or from a consideration of decisions in disputed cases. None of them, however, have strictly the force of law; in fact, some have actually been disclaimed by the bodies to which they were attributed. The proportions are parts per 100,000:—Rivers Pollution Commissioners—Organic carbon, 2·0; organic nitrogen, 0·3. Thames Conservancy—Organic carbon, 3·0; organic nitrogen, 1·1. The Thames Conservancy state that they require a higher standard for effluents just above the intakes of the water companies than for those below. Derbyshire County Council—Albumenoid ammonia, 0·1; oxygen absorbed, 1·0. Ribble Board—Albumenoid, 0·1; oxygen absorbed, 2·0. Mersey and Irwell—Albumenoid, 0·14; oxygen absorbed, 1·40.

Provisos as to amount of suspended solids, acidity, alkalinity, metals, &c., are inserted in some, and have special reference to manufacturing effluents.

But in all these arbitrary limits, no account is taken of the volume of the river into which the effluents are discharged, although attention was long ago drawn to the purifying action of river water. The London County Council have recognised the fact that an oxidising agent added to the effluent at the time of contact with the river prevents any foulness. Provided, therefore, a river is well aërated, or an effluent is well nitrated, or an oxidising agent is supplied in sufficient quantity at the time of contact, an effluent may contain a larger quantity of organic matter than has been sanctioned in the past, and variations in such quantities are permissible under conditions varied in the above way.

In America, from the work of the Massachusetts State Board of Health, Rudolph Hering fixes a limit to the amount of free ammonia permissible in a stream, and finds that if the flow of the stream is less than 2½ cubic feet per second per 1000 persons (or one gallon per minute per person) "an offence is almost sure to arise"; but when the flow is greater than 7 cubic feet per second per 1000 persons, then safety is assured.

"In other words, when the free ammonia is greater than 0·12 part per 100,000 the conditions are probably objectionable." I find that these limits correspond to about 50 volumes of river water to average sewage in this country, and it is obvious that such conditions are only possible under very special circumstances, and the limit is much greater than we have found necessary in England.

Some time ago, in conversation with Mr. Henry Law, we arranged the following formulæ for the conditions of discharge into a stream. The basis I prefer to take is the same as that preferably adopted for waters, viz., 100 litres or 100,000 parts:—

Let X be the flow of the stream in 100 litres per minute.

O = grammes of free oxygen in 100 litres.

S = number of hectolitres of effluent discharged per minute.

M = grammes of oxygen required to consume the organic matter in 100 litres of effluent, as determined by the permanganate test after deducting that required by nitrites.

N = grammes of available oxygen as nitrate and nitrite per 100 litres.

This latter factor requires explanation. Warington, Munro, Gayon, and Dupetit, Adeney, and others, have shown that, always with the help of bacteria, the oxygen of nitrates and nitrites is available for the burning up of organic matter. In my own experiments I have found that the large loss of organic nitrogen noticed so frequently in analyses of sewage in progressive stages of change was not accounted for by the production of nitrous acid, of ammonia, or of nitrogen gas. Gayon and others have observed the formation of nitrous oxide, which, from its solubility and vague reactions, would ordinarily escape observation. Therefore, to be on the safe side, I have allowed for the available oxygen 2 atoms of O for every HNO_3, *i.e.*, N_2O_5 to N_2O, and 1 atom for HNO_2, or N_2O_3 to N_2O.

The quantity of free oxygen in the stream will then be XO, and that required by the effluent will be S(M − N).

Putting C as the ratio between the amount of oxygen in the stream and that which is required to oxidise the organic matter in the effluent,—

$$XO = C(M - N)S.$$

Where there are no nitrates in the fluid,—

$$XO = CMS.$$

If N be less than M, M − N = the deficit of oxygen in the effluent, requiring to be supplemented by the free oxygen in the river, such an effluent will throw a burden on the river, and cannot be considered in a satisfactory state; and it will be a question of volume and other circumstances whether it can be permitted to be discharged at all. Where XO is greater than (M – N)S there will be a chance of the stream dealing with the inflowing liquid; where the reverse is the case the addition must necessarily cause foulness.

In favourable cases, where bacteria and algæ are active, and the oxygen of the river is able by their help to deal rapidly with the incoming residues, the minimum ratio between the volume of the stream and the volume of effluent that could be allowed to be discharged into it would be indicated by the value of C in the above equation, which would also approximately denote how far the population might increase before the proportion would be seriously disturbed.

The minimum figure will be reduced by the nitrites or nitrates of the river water itself, and by the free oxygen which may be present in the effluent. River water may have 90 per cent of its nitrogen oxidised, and, when saturated, contains about 700 c.c., or, approximately, 1 grm. of free oxygen per 100 litres. We may assume that with the almost unlimited exposure and admixture in a flowing river, the common natural bacteria that work the changes are certain to be present. Hence, in theory, comparatively few volumes of a river water are necessary for supplying the oxygen requisite for even a raw sewage after its solids have been removed by filtration or subsidence. From this cause it is a common observation that the dissolved impurity remaining in a stream is a mere fraction of that in the volumes of sewage that have entered it in its upper course.

But from the factor of time, and the inadvisability of denuding the river of its oxygen, which might be only gradually renewed from the air, it is necessary with the raw liquids of sewage to allow a considerably larger proportion of river water than the minimum above calculated. Dupré states that admixture with about 30 volumes of fully aërated river water prevents sewage from becoming foul, and ultimately purifies it. I have found the same result from a less quantity.

Where the organic matter is well fermented, and the liquid advanced in nitrification, as in properly managed septic effluents, the case is far more favourable. Here, in the above equation, N is greater than M, and there is a surplus of available oxygen in the effluent—that is to say, an effluent of this kind not only does not absolutely require any dilution with river water, as containing within itself the elements of its own purification, but by its surplus oxygen is capable of actually improving the river into which it enters. This apparently paradoxical result in cases of polluted streams is paralleled by the effect of the addition of artificial oxidising agents, such as that of manganate of soda to the Thames at Crossness. In healthy effluents the quantity of available oxygen, N, in the above equation, is far higher than could be supplied by any process of mere aëration.

As an example of the application of the formula $XO = C(M - N)S$, we may cite two rivers, the Thames and the Exe:—

	X_6	O.	M.	N.	S.	C.
Thames ..	1100	0·4	4·3	0·23	100	1·08
Exe	47	1·0	6·66	1·16	1·084	7·9

X and S are stated in million gallons.

The formula shows that the Thames with C = 1·08 has so narrow a margin of effective natural oxidation that it has often had to be supplemented, especially in warm weather, by the addition of chemicals. In the Exe, on the other hand, with C = 7·9, there is a large margin for natural purification.

But we cannot, as a rule, throw the burden of the final changes on the stream on account of the time taken and the odours and deposit that generally ensue. On the other hand, an effluent that is in an active state of wholesome bacterial change, under the above conditions of free and potential oxygen, will conform to Adeney's proposed test:—"The limit of impurity to be allowed in a water should be such, that when a given volume of it is mixed with a given volume of fully aërated river water, and the mixture kept out of contact with air, a decided oxidation of the ammonia originally present into nitrous or nitric acid shall be indicated." . . . It will be noticed that this test is practically that suggested by Dupré many years ago. Such an effluent, as experience teaches, if clear and nearly free from odour, may be safely discharged into any river of moderate volume.

THE
ACTION OF LIGHT UPON DYED COLOURS.*

The Report of the Committee presented this year refers to the results obtained during the year 1896-7, in which period a large number of wool and silk patterns, dyed with various natural and artificial *brown* and *black* colouring matters, were exposed to light.

It is with regret that the Committee have to announce the death of James A. Hirst, Esq., in whose grounds at Adel, near Leeds, all the patterns experimented upon since 1892 have been exposed. Mr. Hirst took great interest in the work of this Committee, and the same interest is shown by his son, E. A. Hirst, Esq., who has expressed the pleasure it gives him in being able to aid in the continuation of the work.

The general method of preparing the dyed patterns and the manner of exposing them under glass, with free access of air and moisture, were the same as already adopted in previous years.

Each dyed pattern was divided into six pieces, one of which was protected from the action of light, while the others were exposed for different periods of time. These "periods of exposure" were made equivalent to those adopted in previous years by exposing, along with the patterns, special series of "standards," dyed with the same colouring matters as were then selected for this purpose. The standards were allowed to fade to the same extent as those which marked off the "fading period" in previous years, before being renewed, or before removing a set of dyed patterns from the action of light. The patterns exposed during 1896-7 are, therefore, comparable, in respect of the amount of fading action to which they have been submitted, with the dyes already reported upon.

The patterns were all put out for exposure on July 22, 1896, certain sets being subsequently removed on the following dates:—August 22, September 29, November 5, 1896; May 22, September 6, 1897. Of these five "periods of exposure" thus marked off, periods 1, 2, 3 were equivalent to each other in fading power, whereas periods 4 and 5 were each equivalent to *four* of the first period in this respect; hence five patterns of each colour have been submitted respectively to an amount of fading equal to 1, 2, 3, 7, and 11 times that of the first "fading period" selected—viz., July 22 to August 22, 1896.

The dyed and faded patterns have been entered in pattern-card books in such a manner that they can be readily compared with each other.

The following tables give the general result of the exposure experiments made during 1896-97, the colours being divided, according to their behaviour towards light, into the following five classes: Very fugitive, fugitive, moderately fast, fast, very fast.

The initial numbers refer to the order of the patterns in the pattern-books. The S. and J. numbers refer to Schultz and Julius's "Tabellarische Uebersicht der künstlichen organischen Farbstoffen."

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* Report of Committee, consisting of Dr. T. E. Thorpe (Chairman), Professor J. J. Hummel (Secretary), Dr. W. H. Perkin, Professor W. J. Russell, Captain Abney, Professor W. Stroud, and Professor R. Meldola. (Drawn up by the Secretary). Read before the British Association (Section B), Bristol Meeting, 1898.

In the case of colouring matters requiring mordants, the particular mordant employed is indicated in brackets after the name of the dye-stuff.

The colours marked thus (*) appear to be somewhat faster than the rest of the class in which they are placed.

Brown Colouring Matters.

Class I.—Very Fugitive Colours. (Wool).

The colours of this class have faded so rapidly that at the end of the first "fading period" (July 22 to Aug. 22, 1896) only a very faint colour remains, or it has become very materially altered in hue. At the end of the fifth period (about one year) all traces of the original colour have disappeared, the woollen cloth exhibiting merely a yellowish, brownish, or greyish tint, according to the colour of the original pattern.

Azo Colours.

Wool Book XII.

Basic Colours.—
1. Leather Brown R. Constitution not published.
2. Chrysoïdine AG. From aniline and *m*-phenylenediamine. S. and J. III. 16.
3. Chrysoïdine FF. From aniline and *m*-toluylenediamine.
8. Leather Brown V. Constitution not published.

Direct Cotton Colours.—
1. Titan Brown Y. Constitution not published.
2. Benzo Brown 5R. From primuline and phenylenediamine. S. and J. III. 110.
*4. Cloth Brown (red shade). From benzidine, salicylic acid, and *α*-naphthol-sulphonic acid NW. S. and J. III. 193.
13. Benzo Brown G. From sulphanilic acid and Bismarck Brown. S. and J. III. 273.
25. Hessian Brown MM. From sulphanilic acid, tolidine, and resorcinol. S. and J. III. 278.

Azoxy Colours.

Wool Book XII.

Direct Cotton Colours.—
21. Mikado Brown M. Constitution not published.

Notes.—In the case of Chrysoïdine AG and FF, and Cloth Brown, the colours alter very rapidly during the first "period of exposure," the altered colours then fade more slowly, without any further change in hue.

Class II.—Fugitive Colours. (Wool).

The colours of this class show very marked fading at the end of the second "fading period" (August 22 to September 29, 1896), and after a year's exposure they have entirely faded, or only a brownish, drab, or grey tint remains.

Azo Colours.

Wool Book XII.

Acid Colours.—
1. Resorcin Brown. From *m*-xylidine, sulphanilic acid, and resorcinol. S. and J. III. 163.
2. Fast Brown G. From sulphanilic acid and *α* naphthol. S. and J. III. 165.
4. Acid Brown G. From aniline and *m*-diamido-azobenzene-*p*-monosulphonic acid. S. and J. II. 136.
7. Naphthylamine Brown. From naphthionic acid and *α*-naphthol. S. and J. III. 92.
8. Sulphamine Brown. From *α*-naphthylamine and nitroso-*β*-naphthol-sodium-bisulphite. S. and J. III. 57.
9. Acid Brown R. From naphthionic acid and Chrysoïdine. S. and J. II. 91.
10. Alkali Brown. From Primuline and *m*-phenylenediamine. S. and J. III. 110.
11. Fast Brown 3B. From *β*-naphthylamine-sulphonic acid Br and *α*-naphthol. S. and J. III. 103.

Wool Book XIII.

Basic Colours.—
*1. Chrome Brown RO (Cr). From naphthionic acid and *α*-naphthol. S. and J. III. 92.
*2. Chrome Brown BO (Cr). Constitution not published.
*3. Chrome Brown R (Cr). Constitution not published.
4. Nut Brown. From *m*-toluylene-diamine and *m*-toluylene-diamine. S. and J. III. 174.
*5. Bismarck Brown 2G. From *m*-phenylene-diamine and *m*-phenylene-diamine. S. and J. III. 172.
*6. Leather Brown. From amido-*p*-acetanilide and *m*-phenylene-diamine; products treated with HCl. S. and J. III. 160.
*7. Leather Brown O. Similar to Leather Brown.

Direct Cotton Colours.—
8. Diazochromine BS. Constitution not published.
11. Toluylene Brown R. From sulphanilic acid and Bismarck Brown sulphonic acid.
15. Direct Brown Y. From *m*-amido-benzoic acid and Bismarck Brown. S. and J. III. 275.
19. Cloth Brown (yellow shade). From benzidine and salicylic acid and dioxy-naphthalene (2·7). S. and J. III. 194.
26. Catechu Brown. From Bismarck Brown and *m*-phenylenediamine. S. and J. II. 220.
27. Congo Brown VBB. Constitution not published.
*28. Catechu Brown DDX. Constitution not published.
*29. Catechu Brown DDDX. Constitution not published.
*30. Hessian Brown B. Constitution not published.
*31. Azo Brown. Constitution not published.
*32. Toluylene Brown R. Constitution not published.
*33. Benzo Brown. Constitution not published.
*34. Benzo Brown BR. Constitution not published.
*35. Benzo Brown B. From naphthionic acid and Bismarck Brown. S. and J. III. 274.
*36. Benzo Brown NB. Constitution not published.
*37. Toluylene Brown M. Constitution not published.
*38. Toluylene Brown B. Constitution not published.
*39. Cotton Brown A. Constitution not published.
*40. Cotton Brown N. Constitution not published.
42. Toluylene Brown VO. Constitution not published.
44. Toluylene Brown 2BO. Constitution not published.
46. Benzo Black Brown. Constitution not published.
47. Sulphon Brown R. Constitution not published.
*48. Sulphon Dark Brown. Constitution not published.

Direct Cotton Colours Developed.—
2. Diazo Brown R (extra). Constitution not published. Azotised and developed with *β*-naphthol.
*3. Zambesi Brown G. Constitution not published. Azotised and developed with toluylene-diamine.
4. Diazo Brown G. Constitution not published. Azotised and developed with *β*-naphthol.
5. Zambesi Brown 2G. Constitution not published. Azotised and developed with toluylene-diamine.
6. Diazo Brown Y. Constitution not published. Azotised and developed with *β*-naphthol.
7. Diazo Brown V. Constitution not published. Azotised and developed with *β*-naphthol.
*8. Diamine Brown V. From benzidine and amidonaphthol-sulphonic acid and *m*-phenylene diamine. S. and J. III. 182. Azotised and developed with phenylene-diamine.

Natural Colouring Matters.

Mordant Colours.—
6. Sanderswood (Cr). Pterocarpus santalinus (wood).
7. Barwood (Cr). Baphia nitida (wood).
*8. Ventilago (Cr). Ventilago madraspatana (root-bark).
10. Camwood (Cr).
11. Limawood (Cr) (Cu). Cæsalpinia echinata (wood).
*13. Catechu (Cr). Areca Catechu (extract).

Notes.—Leather Brown and Leather Brown O might almost equally well be classed as "moderately fast" colours. In the first "fading period" they become somewhat greyish in hue, but the altered colour fades very gradually, leaving at the end of a year a fairly good drab-grey colour.

(To be continued).

ORGANIC MATTER IN BURNT CLAYS AT HIGH TEMPERATURES.

By ROBERT MELDRUM, F.C.S.

During many years my attention has repeatedly been attracted to a green or yellowish-green colour which often appears on porous clay ware after being saturated with water and allowed to dry. This colour often appears on terra-cotta, battery cells, crucibles, drain-pipes, fire-clay bricks, and indeed on nearly all kinds of porous clay ware. At first I formed the opinion that it was due to bacteria or microscopical fungi; this view I held till a favourable opportunity presented itself for a practical examination of the matter. For this purpose white battery cells and red terra-cotta which had been fired recently were selected for the experiments. These were coarsely ground, and from 100 to 200 grms. taken and repeatedly treated with fresh distilled water till no reaction was given for sulphates. The water extract, which measured about 700 c.c., had a distinctly yellow colour, similar to a weak solution of bichrome, and had a very strong earthy smell: this was slowly evaporated, during which numerous small bubbles were given off, which I thought to be very characteristic of these extracts. About 2 c.c. of this gas was collected, but no definite information was obtained as to its nature. On boiling the liquid down to small bulk the smell disappeared, which seems to indicate that the odoriferous principle is a volatile substance. It is remarkable that this same colour is evolved from the filtrate from fossil meal and many porous stones. The highly concentrated extract has a bitter taste, but sometimes sweet. The total soluble matter in burnt clay I have found to vary between 2·94 to 25 grains per lb., after drying at 200° C., which consists mainly of calcium sulphate and chloride, sodium sulphate and chloride.

The following results were obtained from samples of burnt terra-cotta:—Total soluble matter, 11·9, 25·3, 2·94 grains per lb. respectively. No. 2 contained 35·91 per cent SO_3, 12·38 per cent CaO, 5·24 per cent $Al_2O_3.Fe_2O_3$, 1·60 per cent insoluble, 14·12 per cent Na_2O; the analysis could not be completed as all the liquor was exhausted. When the extract was evaporated to dryness it still appeared transparent and slightly yellow in colour; on increasing the heat it became opaque and gave off very pungent vapours smelling like burning fats, but with a sweetish smell of burnt sugar; and on further raising the temperature most irritating and dense vapours were evolved, the residue turning black, which did not yield a yellow colour to water, but on heating with HCl gave strong reaction for iron.

A concentrated extract from battery cells was examined with the following results:—$K_4Fe(CN)_6$, no result; $K_3Fe(CN)_6$, no result; KCNS, no result; H_2S, no result; $(NH_4)_2SO_4$, no result; HCl discharged colour, but was recovered by addition of NH_4HO; KI, no result; $SnCl_2$, discharged colour; $AgNO_3$, almost precipitated the yellow colouring matter along with the chlorine, the precipitate being of a flesh colour; pyrogallic acid gave indigo-blue colour, changing to greenish-blue, this being a very delicate reaction; tannic acid gave bluish-black colour, appearing almost black; sodium phosphate, no change; K_2CO_3, no change; the colour was insoluble in 30 per cent benzol and petroleum.

This examination, though very incomplete, is yet sufficient to indicate that the colouring-matter is an organic salt of iron. All these clays were fired for long periods in an oxidising atmosphere of more or less intensity at temperatures of not less than 700° C., though I have obtained similar extracts from fire-clay ware fired at a temperature of over 1000° C. An apparent satisfactory explanation of this is the absorption of products of combustion during the cooling of the red-hot ware; but it must be remembered that ware fired in muffles, and protected as much as possible from these, also yield extracts containing organic matter. It has been observed that several white clays yield these yellow extracts previous to being fired, and it therefore appears that the yellow matter is contained in the raw clay, and that it undergoes little decomposition during the firing.

It is my intention to carry on this investigation, as it seems to me that, if these results can be confirmed, a new field of research will be opened up.

THE CYANOMETRIC ESTIMATION OF SOME METALS.*

By HARRY BREARLEY and HORACE JERVIS.

Since the use of silver iodide as an indicator in cyanometric estimations was proposed, it has been numerously applied in several branches of analytical chemistry.

Harting says that potassium iodide gives a precipitate with silver nitrate in presence of 30,000 parts of water. In the presence of alkaline salts, especially sulphates, and where the silver nitrate is used to form an opalescence with an excess of potassium iodide, the delicacy of the test is very much heightened. Without exaggeration, this form of indicator may be said to exhibit differences equivalent to one part of nickel, copper, silver, &c., in five million parts of solution.

In estimating nickel salts, say, the cyanide is added until the silver iodide clears up; but, in order that this point shall be exactly coincident with the formation of the double cyanide of nickel and potassium, it is necessary to add the reagent more slowly towards the end. It is general, we believe, where the titrations are numerous to add the cyanide with some levity and then go back with silver nitrate. It may be gathered subsequently that such a procedure is not without its advantages. In going back the silver nitrate may be added either to an agitated liquid, in which case the first observable turbidity may deepen on standing, or by superstratifying the silver nitrate, in which case the turbidity may weaken on standing. In pure solutions these differences—which, of course, right themselves on standing awhile—are not very noticeable; in the presence of some reagents, however, they are emphasised, and it becomes necessary, where speed is a consideration, to adhere to one or the other means of reaching the final indication.

The cyanometric estimation of nickel, probably by comparison with the like estimation of copper, has become notable for the levity with which subsidiary reagents, such as alkalis or alkaline salts, may be added. A point in connection with the potassium iodide, however, deserves notice. Large amounts of KI accentuate the difference noted in the last paragraph. On adding KI to a just cleared solution the turbidity will reappear. Our experience is that the indicator is quicker and more delicate the less potassinm iodide there be used in excess of that necessary to form the working turbidity. The depth of turbidity is a matter of taste, but the addition of 2 c.c. of a 2 per cent KI solution for each 500 c.c. solution titrated provides the deepest desirable cloudiness.

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* This paper only partly covers the ground we have mapped out. A temporary but unavoidable delay leads us to present what was already presentable.

The behaviour of nickel and copper salts during cyanometric estimation shows some notable contrasts. The respective behaviour of the two metals in presence of alkalis and alkaline salts has been referred to. It is remarkable that while the theoretical quantity of KCN will complete the reaction with nickel salts, that with copper salts cannot be completed until a considerable excess of the KCN has been added. In presence of nitrates, acetates, tartrates, and sulphates an alkaline solution of copper (chlorides being absent) causes the silver iodide turbidity to blacken and become almost useless; when nickel replaces copper this does not occur. Nickel salts exhibit a peculiarity which, so far as we are aware, has not previously been referred to. The point should be emphasised, on account of the insidious character of the error it may introduce.

Let, say, 50 c.c. of KCN be added to 0·1 grm. of nickel in solution as nitrate or chloride, where about 70 c.c. of KCN is needed to form the double nickel-potassium cyanide. In a minute, or less, a silky crystalline precipitate will begin to form, and in five or ten minutes all, or nearly all, of the uncombined nickel will have been precipitated. Now, as solutions containing unknown amounts of nickel would be titrated carefully and somewhat slowly, it is manifest that to some extent this reaction may take place. The precipitate is soluble in small excesses of KCN, but not very readily so. It is possible, therefore, that when once formed it would escape detection even after the AgI turbidity was cleared up unless it was present in considerable quantities.

An antidote to this undesirable reaction is to be found in ammonium sulphate. A test in all respects like the preceding one, except that ammonium sulphate equivalent to 2 c.c. strong H_2SO_4 was also added, showed only a faint precipitate after standing twenty minutes. Thus, ammonium sulphate serves the double purpose of heightening the iodide turbidity and retarding the formation of the above-mentioned precipitate.

Cyanometric Estimation of Nickel in presence of other Elements.—At one time we thought it reasonable to deduce from the superior behaviour of nickel in so many circumstances, that its behaviour with associated elements would in no case be worse than those exhibited for copper (Chemical News, lxxvi., 291). Our speculations were fouled in attempting the estimation of nickel in presence of aluminium. On this account, and in view of some later work on nickel alloys, we proceeded to observe the interference of some commonly associated elements and to find such means as would overcome them.

The following details are common to each test:—Amount of nickel, 0·1 grm.; interfering metal, 0·05 and 0·1 grm.; excess of ammonia, 10 c.c. (2 normal). The results are summed in the table. The last column (reproduced from Chemical News, lxxvi., 292) shows the percentage error in the like titration of copper. It is feasible to make alkaline with other bodies than ammonium hydrate; the advantageous use of such will be noted in the remarks allotted to each element. Unless otherwise stated, the foreign element was added as a chloride.

Remarks on the Interferences.

Salts of the alkalis (sodium and potassium) and alkaline earths (calcium, magnesium, strontium, and barium) have no appreciable influence, such as is recorded being conceivably due to experimental error. In the presence of those elements (barium, &c.) which form insoluble sulphates, it is advisable to replace the ammonia sulphate, used to deepen turbidity, by a chloride.

Zinc.—It is found that the interference of zinc decreases as the excess of ammonia increases. On the other hand, if the AgI be cleared and then a measured excess of KCN be added, only a portion of that excess can be active to the silver nitrate which is added to reproduce the turbidity. The more cyanide there is added, the more there is remaining unaccountable to the silver nitrate. This latter fact explains why the copper titration, which necessarily involves a much larger amount of potassium cyanide than is necessary to theoretically complete the reaction should suffer zinc to exert an interference equal to 9·5 per cent, while with nickel the interference is only 2 per cent.

Table I.

Metal.	Nickel found.		Per cent error.	Per cent error with copper.	
	0·05 grm. added.	0·10 grm. added.		Soda salts.	Ammonia salts.
Calcium . ..	0·1000	0·1000	0·0	0·0	0·5
Barium	0·0999	—	0·1	0·0	0·4
Strontium ..	0·1000	0·1002	0·2	0·0	0·0
Magnesium ..	0·1000	0·1002	0·2	0·2	0·2
Zinc	0·1015	0·1021	2·1	2·0	9·4
Cadmium ..	0·1002	0·1003	0·3	0·0	2·8
Aluminium ..	0·0970	0·0956	4·4	0·7	0·7
Iron	0·0989	0·0984	1·6	1·3	0·2
Manganese ..	0·0999	0·1002	0·2	3·0	3·1
Chromic oxide	0·0888	0·0834	16 6	2·5	27·0
„ acid.	0·1003	0·0998	0·2	0·4	—
Tin	—	0·1001	0·1	0·3	0·2
Molybdenum .	0·1000	0·0999	0·1	0·2	0·0
Arsenic	0·1000	0·1000	0·0	0·2	0·2
Antimony ..	0·1000	0·1000	0·0	0·4	0·4
Bismuth . ..	0·1002	0·1001	0·1	0·0	—
Lead	0·1000	0·0999	0·1	0·2	0·0
Uranium . ..	0·1002	0·1001	0·1	0·2	0·4
Tungsten ..	0·0999	0·1000	0·0	—	—

The usual acid titration (see "Aluminium") leaves a discrepancy of 1·3 per cent; but if, after adding the cyanide, we replace the ammonia by soda carbonate, then the zinc becomes for the most part precipitated as carbonate, and only a small portion combines with the excess of cyanide and remains in solution. From this point the procedure is:—Filter off the zinc carbonate through a ribbed paper, and to the filtrate add silver nitrate; it is easy to distinguish between the iodide turbidity and the small amount of zinc carbonate which the silver separates from its cyanide combination, and so it is practicable to note—by the readiness with which the superstratified iodide turbidity disappears, when the solution contains only traces of free KCN. At that point, re-pass the solution through the filter previously used. This operation gives a clear solution in which to observe the end-reaction, and also incorporates the stronger cyanide solutions which were left in the paper and precipitate on the first filtration. With a knowledge of the approximate amount of nickel present, the whole process is very easy and very accurate. The normal titration furnishes the required approximation in a few minutes.

Moore (Chemical News, lix., 292) finds that the titration may be performed in presence of zinc if "to a slightly acid solution there be added an excess of sodic pyrophosphate until the precipitate which at first forms is redissolved to a perfectly clear solution." We must admit that the use of this reagent does improve the results, but our experience is that pyrophosphate alone causes the results to be low, and as the tendency of zinc is to give high results, we consider the betterment of the results on using pyrophosphate to be due, partly at least, to compensatory errors.

Cadmium.—The remarks on the good results of zinc and nickel compared with zinc and copper probably apply also to the cadmium interferences. Where the amount of cadmium was so great as to cause serious error, the acid titration along with soda carbonate might be adopted.

Aluminium.—Where a precipitate is formed in the alkaline liquid, the interference was determined by adding a slight excess of cyanide and filtering off an aliquot portion of the clear filtrate. With aluminium, as well as with other bulky precipitates, we found that the interference varied considerably when the operations were performed in duplicate unless they were carried out in a *precisely* similar way, so that where the amount of aluminium is known its influence on the results cannot be safely eliminated by any method of allowances.

The titration may be accurately performed by adding cyanide to a faintly acid or neutral solution and then at once adding the usual excess of ammonia, filtering an aliquot portion of the clear liquid, and going back with silver nitrate. A preliminary test is necessary unless one has some knowledge of the amount of nickel present. As this procedure eliminates the interference of other metals which are precipitated in an alkaline solution, we may briefly refer to it as the acid process.

Lecœuvre has published a process (CHEMICAL NEWS, lxxi., 188) for estimating nickel, in which potassium cyanide is added to the neutral solution of the nickel salt until the precipitate previously formed is just dissolved.

Pyrophosphate of soda is not a good reagent to use for preventing the precipitation of the alumina. In a direct titration it causes the iodide turbidity to clear too soon, and if an excess of cyanide has been added, the successive turbidities formed by the silver nitrate gradually disappear. These observations are in a line with those of Moore (CHEMICAL NEWS, lxxii., 92), who, using the pyrophosphate to prevent the precipitation of iron, finds that "the solution once cleared up often becomes troubled again on standing for a minute. A further addition of cyanide must be given until the liquid is perfectly limpid."

Tartaric also introduces the lagging element, but only in a small degree, and when used in large amounts. It is to be preferred, too, because, where large amounts must necessarily be used, the turbidity temporarily cleared quickly recovers itself, and the titration is very little delayed. One-tenth of a grm. of aluminium may be kept in solution by 1 grm. of tartaric acid or less, and five times this amount does not greatly confuse the end-reaction. It is noticeable that in copper titrations pyrophosphate is the better reagent to use for the purpose of preventing the precipitation of bulky hydroxides of the associated metals.

Test Analyses.—The KCN was standardised in each case in the usual way.

Modification.	0·05 grm. Al present.	0·10 grm. Al present.
Acid titration	0·1002	0·1003
Tartaric acid	0·1000	0·1001

Iron.—In our regular experience with nickel-iron alloys, we have invariably found that a cyanometric estimation in presence of iron was low. In such cases as this, the low results are generally accountable to the precipitated iron carrying down portions of nickel, and—by occlusion in its flocks—preventing the cyanide readily reacting with it. Such an explanation suggests that if carbonated alkali were used the results should be improved, because the precipitate is notably more open and easily reacted with. The ammonium carbonate re-dissolves a little of the precipitated iron, and so tends to retard the filtration. Otherwise the process is very satisfactory. The acid titration may also be successfully adopted.

Modification	0·5 grm. iron present.	0·10 grm. iron present.
Ammonium carbonate ..	—	0·1001
Acid titration	0·1001	0·1003

(To be continued).

ON SOME COMPOUNDS OF TRIVALENT VANADIUM.*

By JAMES LOCKE and GASTON H. EDWARDS.

(Concluded from p. 169).

IN the analysis of the product the carbon and nitrogen were determined by combustion. The vanadium was estimated by titration with iodine and the potassium as sulphate, in a separate portion, after the oxidation of the vanadium to vanadic acid and its removal as lead vanadate (Roscoe, *Ann. Chem.*, *Liebig*, *Suppl.*, viii., 102).

	Calculated for $KV(CN)_6$.	Found.
V	15·74	15·89
C	22·22	21·80
N	25·93	26·36
K	36·11	36·47
	100·00	100·52

This salt forms another member of the series of complex cyanides of the formula $K_3M(CN)_6$, of which the other members as yet known are $K_3Cr(CN)_6$, $K_3Mn(CN)_6$, $K_3Fe(CN)_6$, $K_3Co(CN)_6$, $K_3Rh(CN)_6$, and $K_3Ir(CN)_6$. The crystals obtained were about a millimetre in length, and of a bright scarlet colour. Owing to their instability it was impossible to measure them, and thus determine whether they were isomorphous with the other members of the series. They appeared under the microscope to be rhombic plates, with well-formed domes and base; in polarised light, however, they showed inclined extinction, and are therefore probably monoclinic like the others. In potassium ferricyanide the angle β is 90° 6′.

Potassium vanadicyanide is readily soluble in water, insoluble in alcohol. Its aqueous solution grows turbid within a few minutes, however, but is much more stable when containing some free potassium cyanide. Even in that case it cannot be kept for any length of time. The freshly-prepared solution is at once decomposed by acids, turning green. It gives off a slight odour of hydrocyanic acid, as does the solid salt itself. The solution is at first stable toward alkalis in the cold, but on heating or standing for some time the hydroxide separates out.

The solution yields coloured precipitates with the neutral solutions of various metals, of which the following are the most distinct:—

Ferrous iron	Red-brown.
Cadmium..	Yellow.
Copper	Yellow.
Nickel	Purple.
Manganese	Greenish-yellow.

Silver and mercury salts are reduced by it, with deposition of the metals. None of these precipitates is stable toward acids, and their colour soon undergoes a change on standing.

We have made repeated attempts to isolate the purple precipitate which separates on the first addition of potassium cyanide to the vanadic solution, but without success. The compound, probably vanadic cyanide, is extremely unstable, and on drying yields a green or brown amorphous product, which is obviously a mixture.

The vanadicyanides of ammonium and sodium seem to exist only in solution. Vanadium cyanide dissolves in excess of ammonium cyanide or sodium cyanide, to solutions of the same colour as that of the potassium salt. No crystalline products, however, could be obtained from either solution, either by evaporation or precipitation with alcohol. When the latter is employed the compounds decompose at once, with separation of a thick blue paste.

The properties and reactions of potassium vanadicyanide are of special interest in view of the relative stability of the complex cyanides of the other metals of the group. The only stable compounds of trivalent cobalt are those which contain the metal as a constituent of a complex radical, either positive, as in the cobaltiamines, or negative, as in $K_3CO(CN)_6$, $H_3Co(CN)_6$, &c. The corresponding ferric compounds, *in comparison with other ferric salts*, are somewhat less stable than the cobaltic compounds as compared with simple cobaltic salts. Thus, for example, potassium ferricyanide is less stable, compared with ferric sulphate, than is potassium cobalticyanide when compared with cobaltic sulphate. The

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* From the *American Chemical Journal*, xx., No. 7.

complex manganese derivatives are relatively still less stable. Among the latter is a sodium salt, $Na_2Mn(CN)_6$, but the free acid is unknown. Chromic cyanide yields neither an acid, $H_3Cr(CN)_6$, nor a sodium salt, and ammonium chromicyanide (*Ann. Chem.*, *Liebig*, iii., 163) is very unstable. The chromicyanide solutions, however, are stable towards alkalis even on boiling. In the case of vanadium, neither the sodium nor ammonium salts can be obtained; potassium vanadicyanide is instantly decomposed by acids, with evolution of hydrocyanic acid, and is stable towards alkalis only in the cold. The simple vanadic salts are comparatively stable. Aluminium, which has the lowest atomic weight of all the metals in the group, is precipitated as hydroxide when potassium cyanide is added to its solution, and no cyanogen compounds at all of this metal can be obtained. The tendency to form complex radicals, throughout the entire group, as compared with the tendency to form simple salts, is thus seen steadily to diminish with a decrease in the atomic weights of its members.

Potassium Vanadisulphocyanate, $K_3V(CNS)_6\,4H_2O$.—Among the characteristic compounds of trivalent chromium the derivatives of chromic sulphocyanate are very prominent. Potassium chromisulphocyanate, $K_3Cr(CNS)_6.6H_2O$, is almost as stable as the chromicyanide. It is not decomposed by either alkalis or acids in cold solution (Rösler, *Ibid.*, cxli., 185). A number of other salts, such as $Ag_3Cr(CNS)_6$, $Ba_3[Cr(CNS)_6]_2$, &c., derivatives of the same acid, $H_3Cr(CNS)_6$, are also known.

We have succeeded in preparing a compound of vanadium analogous to this potassium salt, and find that it corresponds very closely to the latter in its reactions. The method employed was as follows:—

An alcoholic solution of potassium sulphocyanate was made by fusing sulphur with potassium cyanide (*Chem. Zeitung*, 1866, 666), digesting the product with absolute alcohol, and filtering. To this solution was added somewhat less than the calculated quantity of vanadium chloride, dissolved in a small volume of water. A precipitate of potassium chloride at once appeared, and the solution assumed a deep brown colour. After digestion for an hour on the water-bath the solution was concentrated by evaporation, and then placed in a vacuum-desiccator to crystallise. The first crop of crystals consisted of a mixture of about equal proportions of potassium sulphocyanate and vanadisulphocyanate. This was removed, and the evaporation continued until the solution was of a thick syrupy consistency. A large quantity of homogeneous, dark red crystals, almost black, were thus obtained. They were cleaned as thoroughly as possible by pressure between filter-paper, washed with ether, and dried in a vacuum. The analysis gave the following results:—

	Calculated for $K_3V(CNS_6).4H_2O$.	Found.
K	19·90	19·52
C	12·24	—
N	14·29	14·73
S	32 65	33·23
V	8·68	8·55, 8·22, 8·79
H_2O	12·24	13·09
	100·00	

Potassium vanadisulphocyanate, like the corresponding chromium salt, is extremely soluble in both alcohol and water, but is stable only in presence of an excess of potassium sulphocyanate. The pure salt is decomposed by either solvent, forming a green solution. Crystals mixed with a small quantity of sulphocyanate are very hygroscopic, dissolving in the water absorbed. Toward oxygen the salt is the most stable of any which we have prepared. The vanadium in the radical $V(CNS)_6$ undergoes oxidation only very slowly, and in presence of potassium sulphocyanate the solution may be left exposed to the air for some time without losing its characteristic dark brown colour. Alkalis precipitate vanadic hydroxide from the solution only on boiling, but it is at once decomposed by acids.

The preparation of corresponding salts of other metals, such as $Na_3V(CNS)_6$, $Ba_3[V(CNS)_6]_2$, &c., we have not yet attempted, but we hope to do so in the near future. Our investigations on the vanadic compounds in general will be continued.

ON THE
TRANSFORMATION OF CHEMICAL ENERGY INTO ELECTRIC ENERGY.*

By Prof. F. FOERSTER.

The number of galvanic elements prepared and used for different purposes is very considerable. Several of them, such as the Daniell cell modified by Meidinger, have been extensively used for the production of small currents. But their adoption for the production of large currents would be too expensive, since they require and use up quantities of expensive material, such as zinc for example. On the other hand, all efforts to increase the electromotive force of galvanic cells have met with very little success, and we now know, thanks to the remarkable theory of Nernst, that the nature itself of these cells will not allow of the electromotive being raised to more than 2 or 3 volts. It is therefore necessary to find a substance as cheap as possible if we wish to produce commercially an electric current by means of a galvanic battery; carbon has long been thought of,—its potential energy already serves as the source of power in most industrial undertakings.

The problem of the oxidation of carbon or of its commercial compounds, in galvanic cells in the cold, so as to obtain its potential energy in the form of an electric current, has occupied the attention of electricians for more than twenty years, and has formed the subject of innumerable patents. The most interesting of the earlier researches on this subject were recently published in a review in the *Zeitschrift fur Electrochemie* (vol. iv., pp. 129 and 165). The great importance of this problem was demonsrated by Ostwald in 1894 in an address delivered before the general assembly of the German Electrochemical Society (*Zeit. f. Elect.*, i., pp. 81 and 122), and it still holds good up to the present. If we compare the number of electrochemical processes introduced commercially with the number of those which have been proposed, and which might have a certain value, we see that the first-named form has only an insignificant minority, and this is due more than anything to the high price of the electric energy. In places where hydraulic power is obtainable,—such as in the Alps, in Norway, Sweden, at Niagara, and latterly also on the Ebro, a river which has a very rapid current,—the electrochemical industry has commenced to develope, for under such conditions electric energy is comparatively cheap. But if we are obliged to produce the electric energy from coal, by burning it to form steam, and transforming the energy of the steam into mechanical energy, the final utilisation of the energy in the carbon is very incomplete. To begin with, the transformation of the heat of combustion of the coal into mechanical work by the aid of furnaces, boilers, and engines, gives a loss of 85 to 86 per cent of the total energy.

It is therefore clear that this return is much too expensive for a large number of chemical processes which, however, employ carbon directly. But it would be quite otherwise if we could transform the latent heat of the coal directly into electric energy by its combustion in the

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* *Moniteur Scientifiquv*, Series 4, vol. xii., July, 1898.

cold in galvanic cells; under such circumstances we might be quite content to utilise only one-third, or even one-half, of the energy.

Since carbon in the state of coke or gas carbon is a good conductor of electricity, it appears rational at first sight to use it in one of these forms as the soluble electrode in the galvanic cell. A very simple element of this nature was made by M. Cochu (*Zeit. f. Elect.*, ii., p. 541). It is based on the well-known fact that carbon can be kept in solution by concentrated sulphuric acid, especially when hot. Cochu plunged the coke or gas carbon into sulphuric acid, using a plate of peroxide of lead as the source of oxygen. The cell, closed through a resistance of 100 ohms, possesses an electromotive force of 1·03 volts, and the current continues until the complete reduction of the peroxide of lead.

We have heard nothing further of this cell. To give it a practical value it would be necessary to replace the peroxide of lead by an electrode which would not be attacked, near which a current of air would play the oxidising part of the peroxide.

Jacques (*Zeit. f. Elect.*, ii., pp. 604 and 4130) attempted to make a carbon cell on another principle. He plunged the carbon into melted caustic soda contained in an iron crucible heated externally. Air was blown into the melted mass below the carbon. A current was established between the carbon and the iron in the interior of the cell. By using large external resistances an electromotive force of 1 volt could be obtained.

Nevertheless we can see that the Jacques cell does not affect the problem we have before us. In this case it would be necessary to direct the current of energy towards the iron and not towards the carbon, since the general principle of the construction of galvanic elements requires that the materials whose reaction serves as the source of electric energy should not mix, but remain separate one from the other: this is a condition necessary for the transformation of chemical into electrical energy. Thus the precipitation of salts of copper by zinc can only produce a current when the zinc is out of the solution of sulphate or other cupric salt. This is the case in the Daniell cell.

It is the same with several other processes,—for example, with those when the oxidation of the carbon is effected by the aid of a melted nitrate. It would be superfluous to mention them all in this article; and, further, I should not have described the cell made by Jacques if—thanks perhaps to the claims put forward—there had not been several interesting researches carried out on the subject, which have thrown a good deal of light on the nature of galvanic cells with melted electrolytes.

Andrews (*Zeit. f. Elect.*, iii., p. 117) and Reed (*Ibid.*, iii., p. 121) first thought that the Jacques cell constituted a species of thermoelectric element, since the iron is heated externally, while the carbon is cooled by the air. This opinion seemed to be confirmed by an experiment which showed that the electromotive force of the Jacques cell varied according to the difference of temperature of the two electrodes, and that the same phenomena could be reproduced when the carbon was replaced by certain metals. However, all the phenomena could only be produced irregularly, which led Andrews to suppose that the thermoelectric phenomena were here accompanied by electrochemical reactions. Latterly Liebenow and Strasser have succeeded in throwing light on these very remarkable reactions, and in showing that they constitute the principal source of the electromotive force in the Jacques cell (*Ibid.*, iii., p. 353). If we plunge rods of iron, nickel, or silver into melted potash, putting them in connection with a normal electrode, it will be seen that from the commencement they have a negative potential, and that the nickel dissolves in the potash with the evolution of hydrogen; but after some time a reaction followed by the absorption of heat suddenly takes place, and the potential between the metal and the electrolyte becomes 1 volt less negative than before; the oxygen of the air has oxidised the molten mass, and the metal is now passive. Carbon also dissolves in melted potash, giving off hydrogen; it, however, does not become passive, but keeps its potential, which is about the same as that of iron at the commencement of the reaction. Thus if we simultaneously plunge iron and carbon into melted potash through which the oxygen of the air has free passage, we obtain an electromotive force of 1 volt as soon as the iron has become passive. The air blown in first makes the iron passive, and then depolarises the carbon, driving off the disengaged hydrogen.

The Jacques cell works by consuming caustic potash, and consequently does not in any way affect the problem set above. Its electromotive force increases slightly with the rise of temperature; this partly explains the results found by Andrews and Reed.

If we examine the processes which require carbon as the soluble electrode more closely, we can easily see that they have no chance of effecting the complete solution of our problem. On the one hand, the ash from the carbon would soon interfere very considerably with the action of the cell, and, on the other hand, the carbon should be made a very good conductor of electricity, which is very difficult with certain kinds of carbon, and besides is always very expensive.

These difficulties have given rise to the idea of replacing the carbon in its natural state by certain gaseous products which can be obtained, notably by means of carbonic oxide, and perhaps also by hydrocarbides which would be brought into contact with the insoluble electrodes to burn them into carbonic acid. At first sight the choice of this method does not seem to be very advantageous, since the ordinary combustion of carbon to carbonic oxide is accompanied by a considerable loss of potential energy in the state of heat.

We know that the formation of a gramme-molecule of carbonic oxide by the combustion of carbon gives 29,000 calories, while the final oxidation of carbonic oxide into carbonic acid is accompanied by the disengagement of 68,000 calories. But the first part of the energy is in no way lost for the production of the electric current. We know that this energy represents exactly the heat necessary for effecting the decomposition of water by carbon, $H_2O + C = CO + H_2$, and which is consequently refound in the potential energy of the hydrogen and the carbonic oxide. That is precisely the basis of the commercial production of water-gas. In the last place it will be necesssary to bring this gas into the carbon cell. We shall see directly that the presence of hydrogen cannot be but advantageous.

As for the construction of such a cell, it must have the form of a gas element. This interesting type of galvanic element was discovered by Grove, who showed that two strips of platinum, charged electrolytically the one with hydrogen and the other with oxygen, plunged into dilute sulphuric acid, gave birth to an electric current which passes through the acid from the hydrogen to the oxygen. The phenomenon is produced far better if the two strips have been previously platinised by an electrolytic deposit.

In what now follows we must suppose the element of the Grove type of cell to be of the following form:—Two vertical glass tubes opened at the lower end and closed on the top, plunged into dilute sulphuric acid; two strips of platinised platinum are introduced, one in each; the tubes are charged, one with hydrogen and the other with oxygen. If now we connect the two strips by means of a wire, we find a current of 1·07 volts passing through the wire. At the same time the volume of both the gases diminishes, that of the hydrogen going twice as fast as that of the oxygen; the electric current ceases when the gas has completely disappeared.

This interesting phenomenon is explained in the following manner:—The oxygen by its solution in water tends to form negative ions O [according to Nernst (*Berichte*, xxx., p. 1555) the water will contain, besides the ions OH, other ions O, and it is these latter that probably here play the principal *rôle*]. Perhaps a very small number of the atoms of oxygen to be found in the platinum become transformed into ions; but this transformation cannot take place without an equivalent quantity of positive electricity being spread over the platinum, and between this electricity and the negative charges of the oxygen ions there would be an attraction.

But this attraction would disappear if the positive electricity of the platinum could be otherwise directed. This is what takes place in our experiment:—The positive electricity of the platinum diffuses, by means of the wire, to the second platinum strip which is in contact with the hydrogen. This, on becoming charged with positive electricity, gives hydrogen ions, and it is thus that the two gases become transformed into ions of water and remain in the electrolyte,—that is to say, in the sulphuric acid. In this manner we find ourselves in the presence of a combustion of hydrogen in water, in the cold.

In a carbon cell the hydrogen ought to be accompanied or replaced by carbonic oxide, or perhaps by hydrocarbides. The sulphuric acid ought to give place to another electrolyte which would allow these carbon compounds to change into positive ions, and to combine with the oxygen ions, giving water or carbonic acid.

(To be continued).

A TABLE OF ATOMIC WEIGHTS.*

By THEODORE WILLIAM RICHARDS.

Since no natural constants are more used by chemists than the atomic weights, it is a matter of great importance for every one, from the chemical philosopher to the practical analyst, to have a convenient table of them always at hand. Unfortunately the present state of our science makes the selection of the values often a matter of personal opinion; and because this is the case, it is well that many of those who have had experience in accurate quantitative analysis should express their views. Hence arose the present work, which was begun solely for use in Harvard College.

It is true that an accurate table of atomic weights may sometimes be less appropriate for the calculation of analyses than an inaccurate one, for the constant errors of any one process are eliminated as much as possible from the accurate table, and, moreover, all the results are reduced to the vacuum standard. Of course neither of these refinements is to be expected in common work, although many uncorrected methods may yield results which are very consistent among themselves. Obviously the best table for the practical calculation of analyses would be a list of factors, in which each quantity had been found empirically according to precisely the method which is to be employed in the analysis of an unknown substance (compare Seubert, *Ber. d. Chem. Ges.*, xxi., 2180). Since, however, the errors of ordinary work often eliminate one another, and, since such a table of empirical factors would have to be accompanied by exceedingly minute directions, the scientifically accurate table of atomic weights is generally the most convenient substitute for the factors demanded by the analyst, as well as the most suitable basis for theoretical considerations concerning the periodic system of the element.

In the compilation of the accompanying table the chief emphasis has been laid on the probable chemical accuracy of the processes involved in each case. The search for possible causes of constant chemical error has usually furnished the evidence, if any evidence was to be obtained, upon which has been based the sometimes very puzzling decisions between conflicting data. For example, the possible occlusion of foreign matters by many precipitates has always been borne in mind, as well as the fact that crystals obtained from aqueous solutions usually retain with great obstinacy important amounts of mother-liquor enclosed within their structure. Oxides and other substances obtained by ignition often have a tendency to occlude traces of other materials remaining from their mother compound; of course the possibilities of such a serious error must be carefully weighed in each case. Most experimenters upon the volumetric ratio of silver to the chlorides have produced erroneous data, through lack of knowledge of the dangers of this apparently simple process. These results must then be given small weight, no matter how concordant they may seem. The solubility of glass and porcelain, as well as nearly all precipitates, is another frequently overlooked source of grave complications, and so is the action of many substances upon their containing vessels at high temperatures. The fact that in some cases the necessary methods of calculation greatly magnify the experimental error was not forgotten. These and many other equally obvious minor principles have served as the guides in the selection of the figures below; but of course the results cannot be considered ultimate. "Post-mortem examinations are often unable to detect the more subtle poisons." In many cases much more experimental work is needed, not only to secure new data, but also to show where the old are in error. While, however, it is very important to show such falsity, the attempt to counteract it numerically by the application of small corrections is a dangerous remedy; for minor conditions often seriously modify the minor corrections. In such cases wholly new data must usually be obtained, and these must be corrected, if correction is necessary, by him who is familiar with every step of the processes involved.

One is continually reminded, as he studies the conflicting evidence of the words of Ostwald:—"Differenzen sind nicht selten, und mahnen ernstlich an die Unvollkommenheit menschlicher Arbeit, aber auch an die Verantwortung welcher jeder übernimmt, welcher einen numerischen Wert der Oeffentlichkeit mitteilt" (*Ztschr. Phys. Chem.*, iii., 143). This responsibility is not always realised by eager investigators, who seek to make up for a possible lack of quality by a superabundance of quantity. "A single determination, well worked out, is better than twenty incomplete ones. Too much cannot be said against the multiplication of incomplete or carelessly obtained data; for such data carry with them not only uncertainty and confusion in the present, but also additional labour for a reviser in the future" (*Proceedings Amer. Acad.*, xxxi., 99; xxvi., 294). Every reaction must be assumed to involve some constant error, and every substance must be assumed to contain some constant impurity, until a proof of the contrary is obtained. Our wofully discordant data furnish a heavy presumption against almost any chemical method, when greater accuracy than one part in four or five hundred is desired.

The standard O = 16·000 is adopted below, as likely to be the most convenient for many years to come (compare F. W. Küster, *Ztschr. Anorg. Chem.*, xiv., 251). The last figure of each number given in the following table cannot be considered in any case certain. It is often probably not much more than one unit in error, although the uncertainty may amount to as much as six or eight units in some cases. Of course the decimal notation does not admit of closer indications without an individual explanation in each case. For example:—Iron, germanium, and gallium are given in the table as 56·0, 70·0, and 72·5 respectively. The first is probably known within 0·1 or 0·2, while the other two may easily be 0·5 in error; but the method of expressing the results does not admit of this grade of distinction.

The aim has been to construct a convenient working table, which shall carry with it all that is trustworthy, and nothing that is unnecessary. It is almost needless to state that the well-known standard works of Clarke, Meyer and Seubert, Ostwald, Van der Plaats, and others,

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have been freely consulted in the preparation of this table, as well as many of the original papers.

Especially am I indebted to Professor Clarke for his latest gigantic collection of data and results (Smithson, "Misc. Coll. Constants of Nature," v., 1897), which would have made the present table a work of supererogation, if he had viewed the subject from a somewhat less mathematical standpoint. Professor Clarke's method of decision places the credit with the skilful manipulator; I have striven to give the thoughtful chemist who is not so clever with his hands the credit which I think belongs to him. The fact that the two tables usually agree is due either to the best methods having fallen into the best hands; or to Professor Clarke's having wisely forsaken the rigid application of his principle; or else, especially in the case of the rare metals, to the lack of data affording room for intelligent difference of opinion. Among the seventy-four atomic weights given in the table, only seven differ enough from the values computed by Clarke to excite remark. It seems fitting to give a brief statement of the reasons for the differences in those seven cases, leaving the details of reasoning about the other sixty-seven elements unpublished. The elements mentioned are antimony, cadmium, calcium, magnesium, platinum, tungsten, and uranium.

It is not my purpose to enter at length into the discussion of the antimony problem. Much of the voluminous work upon this subject is now rejected by common consent. The work of Bongartz (*Ber. Chem. Ges.*, xvi., 1942, 1883), sometimes accepted as the best because it is the most recent, has the grave faults inherent in all methods which involve the precipitation of baric sulphate. Among all the published data Cooke's analyses of antimonious bromide (*Proc. Am. Acad.*, v., 13, 1877), Sb = 119·92, seem to me the most satisfactory, because of the admirable fitness of argentic bromide for quantitative work, and because of the many precations used in both preparation and analysis. Cooke's and Schneider's (*Pogg. Ann.*, xcviii., 293, 1856; *Jour. Prakt. Chem.*, [2], xxii., 131, 1880) work upon the sulphide, Sb = 120·5, are perhaps the next in order; but Cooke's work upon this subject was far less satisfactory than his work on the bromide. Accordingly the value 120·0 is given as the atomic weight of antimony in the accompanying table, instead of 120·43, computed by Clarke.

Although the atomic weight of cadmium has been the subject of many investigations, it is still far from certainly established. Many reasons combine to make me think that the highest of the published values are the most accurate. Dumas's (*Ann. Chem., Liebig*, cxiii., 27, 1860) work upon the chloride of cadmium led to the value 112·23; but his method of investigating chlorides sometimes gave him too low results (see *Proc. Am. Acad.*, xxx., 371; cases in point—barium, strontium, sodium, and tin). V. Hauer (*Jour. Prakt. Chem.*, lxxii., 350, 1857) and Partridge (*Am. Jour. Sci.* [3], xl., 377, 1890) found cadmium equal to less than 112 by heating cadmic sulphate in a stream of hydric sulphide, but there is no proof that their initial substance was thoroughly dried. On the other hand, Bucher's conversion of cadmic sulphate into the oxide led to the value 112·36, which Bucher regards as the minimum ("Johns Hopkins Inaug. Dissertation, Baltimore, 1892"). This method is one in which the tendency of the oxide to retain sulphuric acid is approximately neutralised by the tendency of the sulphate to retain water: this fact is demonstrated by Baubigny's (*Comptes Rend.*, xcvii., 906, 951, 1369; 1883) good results on zinc, nickel, and aluminium, as well as Marignac's (see under Magnesium, later in this paper; compare *Proc. Am. Acad.*, xxvi., 260, 273; xxxi., 160) on magnesium. The results of Lenssen (*Jour. Prakt. Chem.*, lxxix., 281, 1860), Partridge, Morse and Jones (*Amer. Chem. Journ.*, xiv., 260), and Bucher, involving the use of cadmic oxalate, all in the neighbourhood of 112, are likely to be too low because of the great difficulty of freeing this substance from water. Morse and Jones have clearly indicated this and other possible causes of error. Moreover, I doubt very much if it is possible to prepare the oxalate free from the nitrate by precipitation from solutions containing cadmic nitrate. The method of calculation magnifies either error by introducing it in opposite directions into the numerator and denominator. Bucher's extended work casts grave doubts upon cadmic oxide (used by Morse and Jones, and Lorimer and Smith) (*Ztschr. Anorg. Chem.*, i. 364) as a suitable substance to serve for a basis of operations. On the other hand, the work of Huntington (*Proc. Am. Acad.*, 1881, p. 28) and Bucher with a bromide (a very satisfactory substance as to its preparation because it may be sublimed, and as to its analysis because of the insolubility of argentic bromide), and that of Bucher with calmic chloride, point toward 112·3 or 112·4 as the probable figure. The electrolytic work of Hardin (*Journ. Am. Chem. Soc.*, 1896, xviii., 1016) upon these compounds, performed unfortunately with small amounts of material, is nevertheless in favour of the lower value, 112·0, so that any value adopted must be uncertain. Clarke computes 111·95; for the accompanying table 112·3 has been chosen.

There is good reason for believing that Clarke's value for calcium (40·07) is probably too high. The only determinations worth considering are those of Erdmann and Marchand upon the composition of Iceland spar, and only one out of their thirteen experiments is corrected for known causes of constant error (*Journ. Prakt. Chem.*, xxx., 257, 1850). This experiment, which really constitutes the sum and substance of our pseudo-accurate knowledge of a very important quantity, makes calcium almost exactly 40·0. Obviously but little confidence may be placed in such meagre material; it is surprising enough that so common an element has remained forty years untouched on so unsatisfactory a basis. An extended investigation, now well advanced in this laboratory, has as its object the securing of less impeachable data upon the atomic weight of this frequently appearing constituent of the universe.

Marignac's results (*Arch. Sci. Phys. et Nat.*, [3], x., 206) from the quantitative ignition and synthesis of magnesic sulphate, processes in which the constant errors are likely to eliminate one another, have been so completely confirmed by the recent work of Richards and Parker (*Proc. Am. Acad.*, xxxii., 53; *Ztschr. Anorg. Chem.*, xiii., 81, 1896) that magnesium is represented by the figure 24·36 in the table. The results of the syntheses of magnesic oxide by Burton and Vorce (*Amer. Chem. Journ.*, xii., 219, 1890) have been shown by Richards and Rogers (*Proc. Am. Acad.*, xxviii., 200) to be under the cloud of a serious possible constant error, and no other results offer weighty evidence against the value just named.

(To be continued).

Preventive of Rust on Metal Work.—Lard 125, camphor 20, are melted together and a little graphite added. The objects are dressed with this paste, which is removed after twenty-four hours.

Banquet to Past Presidents of the Chemical Society.—The banquet of the Chemical Society to those of its Past Presidents who have completed fifty years' Fellowship of the Society, which was postponed last June owing to the lamented death of the Senior Past President, Lord Playfair, is now arranged to take place on Friday, November 11, at the Hotel Métropole. The Past Presidents who will then be entertained are:—Sir J. H. Gilbert, F.R.S.; Sir Edward Frankland, F.R.S.; Professor Odling, F.R.S.; Sir F. A. Abel, Bart., F.R.S.; Dr. A. W. Williamson, F.R.S.; and Dr. J. H. Gladstone F.R.S.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvi., No. 24, June 13, 1898.

Spectral Researches on the Atmospheric Air.—H. Moissan and H. Deslandres.—Already inserted.

On the Mixture of Gases.—D. Berthelot.—The author reviews the results obtained by previous workers on the subject, such as Dalton, Amagat, Sarrau, Leduc, &c., with regard to the densities and pressures of gaseous mixtures. He goes on to show in a long mathematical paper that previous theories are not tenable, but that the one he has developed is the only one which will in every case agree with experiment.

Atomic Weight of Nitrogen.—M. Vèzes.—The comparison of the atomic weights, calculated according to the method given by M. Berthelot, with the atomic weights found by chemical analysis gives a very satisfactory concordance for certain elements (hydrogen, carbon), while with certain other elements (chlorine, sulphur, phosphorus, and above all nitrogen) it shows a considerable divergence. Taking the atomic weight of oxygen as 16·000, we get for hydrogen, from the physical observations of M. Berthelot, 14·005, and by chemical analysis (Stas) 14·044. The divergence between these two numbers is, as can be seen, nearly three-thousandths of their value. Berthelot explains this difference by a systematic error which vitiated the results of the classic work of Stas. This error was first pointed out by Dumas, who showed that the granulated silver used by Stas retained a certain amount of oxygen which was dissolved during its fusion. But this point was answered by Stas in a paper published after his death, and according to his calculations the atomic weight of nitrogen would be—

Stas	14·044
Corrected value	14·040

The systematic error pointed out by Dumas does not, therefore, hold good.

Atomic Weight of Tellurium.—R. Metzner.—The determination of the atomic weight of tellurium has been the subject of numerous researches. The latest results give figures comprised between 127·05 and 127 74. The author's experiments were carried out according to the two methods which appeared to be the most to be relied upon. First, the use of sulphate of tellurium, and, secondly, the reduction of tellurous acid; the results of all the experiments have given him numbers higher than those of Brauner and Staudenmaier, the mean of his results being 127·9.

Action of Sodammonium in excess on Red Phosphorus.—C. Hugot.—The results of the action of phosphorus in excess on sodammonium has already been published (*Comptes Rendus*, cxxi., p. 206). The action of sodammonium in excess on phosphorus gives rise to a compound which is fully described in this paper. A yellow body is formed corresponding to the formula $P_2H_3Na_3$; this yellow body treated by acids and water gives rise to the following reactions:—

$$P_2H_3Na_3 + 3HCl = 3NaCl + 2PH_3$$

and

$$P_2H_3Na_3 + 3H_2O = 3NaHO + 2PH_3.$$

Heated in vacuo the body $P_2H_3Na_3$, after having lost the little ammonia gas it contains, gives off at about 100° phosphide of hydrogen and a little hydrogen; on increasing the heat the proportion of these two gases given off changes, until at 200° to 300° nothing but hydrogen is collected.

Preparation and Properties of a New Carbide of Tungsten.—P. Williams.—Already inserted in full.

New Method for the Separation of Geraniol and Citronellol.—J. Flatau and H. Labbé.—The authors describe how they have prepared a certain quantity of ethers from the two alcohols. The product obtained is washed very carefully with carbonate of soda, and then fractionated in vacuo. After several distillations the ethers are precipitated from the alcohols in excess; by titration 98 per cent of pure ether is found. Both these ethers possess a very agreeable odour.

MISCELLANEOUS.

Glasgow and West of Scotland Technical College. —*Prize of £30 and Research Studentship in Chemistry.*—The Directors of Nobel's Explosives Company, Limited, after consultation with Dr. G. G. Henderson, Freeland Professor of Chemistry in the above College, have decided to give a prize tenable under the following conditions:—

(1). The prize to be £30, and to be known as the "Nobel Company Prize."

(2). The prize to be awarded annually, until further notice, to a student in the chemical laboratory of the Technical College who has passed through the usual course of training in that laboratory, and who, in the opinion of the Professor of Chemistry for the time being, is qualified to prosecute research.

(3). The holder of the prize to engage in research work in the chemical laboratory of the Technical College, under the direction of the Professor of Chemistry for the time being, for the period of one academical year, viz., from beginning of October until middle of July.

(4). The prize to be awarded by the Professor of Chemistry for the time being, but to be withheld in any year if there is at that time, in his opinion, no student in the chemical laboratory with the necessary qualifications.

It was also suggested by the Directors "that, while not making it a condition of the gift, the prize might be awarded by preference to a student who would be willing to accept it on the understanding that the Company would have the first call on his services, on terms not less favourable than those he might secure elsewhere." In accepting the gift on the above terms the Governors of the College further resolved to grant a free studentship for one year in the laboratory to the Nobel Company's Prizeman, thus raising the money value of the prize to about £50. The example of Nobel's Company might profitably be followed by other chemical manufacturers.

THE CHEMICAL NEWS.

Vol. LXXVIII., No. 2029.

DALTON'S LAW.*

By W. N. SHAW, F.R.S.

Discrepancies between the sum of the partial pressures of air or nitrogen and saturated vapour and the pressure of mixtures of the gases respectively with saturated vapour, indicating *prima facie* a departure from Dalton's law, were shown by Regnault (*Ann. de Chim.*, [3], vol. xv.) to exist for water vapour: the extent of the difference being on the average nearly half a millimetre.

Regnault himself, in his classical paper on the Pressure of Vapours (*Mem. de l'Institut*, vol. xxvi.) sought to throw additional light on these discrepancies by examining the increase of pressure produced by adding ether or some other volatile liquid to an atmosphere, the pressure of which had been previously measured. In the course of these experiments, he concluded that he had satisfactorily ascertained the cause of the phenomena to be the condensation of the vapour on the vertical sides of the containing tube under a pressure of vapour less than the saturation pressure corresponding to the temperature. He regarded Dalton's law as being true, in fact, for a gas-filled space completely surrounded by a sufficiently thick layer of the evaporating liquid. In a vessel with solid vertical walls gravity prevents the formation of a layer of the required thickness on the vertical sides. This hypothesis was held to account for the fact that, if the mixture were compressed as in a Boyle's law tube, the pressure gradually diminished after the initial compression to a value less than that required by Dalton's law; in the case of ether about 10 m.m. of pressure were missing on this account.

Such a hypothesis would give a satisfactory explanation of the phenomena if the sides of the glass vessel were gradually dissolved away by the liquid condensing, as, for example, would be the case if the tube were made of rock salt, but if the action between the glass sides and the vapour were merely a mechanical one, the supposed continuous evaporation of liquid from the horizontal surface and its return to the stock by condensation on the vertical sides, and running down these, would seem to contradict the principle of conservation of energy.

Regnault's explanation is the more difficult to accept if the density of the vapour be considered. Prof. J. J. Thomson, in his "Application of Dynamics to Physics and Chemistry," has shown that the addition of air-pressure upon a liquid surface in contact with its saturated vapour ought to result in a slight additional evaporation, causing a slightly increased density of vapour, and the experiments of the author upon air at various degrees of saturation (*Phil. Trans.*, 1888) indicated some slight increase of density beyond that required to correspond with the vacuum pressure, so that any departure from Dalton's law could not be attributed to the want of mass of vapour in the saturated air.

The point might be investigated by examining closely the behaviour of a mixture of air and vapour under isothermal conditions in the neighbourhood of the point at which condensation begins to occur. At great rarefaction the mixture would behave as a perfect gas, and if the isothermal relation between p and $1/v$ were plotted on a diagram (with a suitable correction if necessary for the deviation of the air from Boyle's law) the curve obtained would be a straight line through the origin represented by $p=k\times 1/v$. At great concentration, if Dalton's law were strictly true, the relation would again be represented by a straight line, viz., $p=k'\,1/v+p_v$; where k' is the Boyle's law constant for the contained dry air, and p_v is the saturation pressure of the vapour. This line would cut the vertical line $1/v=0$ in the point distant p_v (*i.e.*, the theoretical saturation pressure) from the origin, and it would cut the line $p=0$ in the point $1/v=-\frac{p_v}{k'}$. These two theoretical lines would meet if produced at an obtuse angle in the theoretical saturation point.

If, on the other hand, at the greater concentrations there were a discrepancy from Dalton's law proportional to the total pressure and therefore represented by the relation $p=k\times 1/v+p_v-\lambda p$, the observations would still show a straight line not quite coinciding in direction with the theoretical line for Dalton's law, but cutting that line in the point on the horizontal axis $(-p_v/k',\,0)$, and cutting the vertical axis at a point distant $p_v/(1+\lambda)$ from the origin. Various other hypothetical laws of variation might also be suggested.

A series of observations thus plotted would enable one to determine whether the actual behaviour tended to approach agreement with Dalton's law, or some recognisable modification of it, such as that suggested.

Regnault's observations, recorded in the paper referred to, include a series of determinations of the pressure and related volumes of mixtures of air and ether vapour for the temperature 7·7° C. They also show the dry air pressures for the series of observed volumes, so that the pressure of this mixture can be plotted against the pressure of dry air for the same volume, and the correction for any deviation from Boyle's law for dry air is thereby made automatically. A diagram showing two sets of his observations was exhibited. The pressures ranged between 600 and 1400 m.m. It was pointed out that, for the observations at greater rarefactions, the theoretical line was very strictly adhered to until the pressure reached 80 per cent of saturation, then slight discrepancy in the direction of loss of pressure was indicated, increasing until it amounted to more than 10 m.m. for the theoretical saturation point; beyond that the discrepancy showed a slightly diminishing value. A straight line drawn to show a theoretical defect from Dalton's law amounting to λp (where $\lambda=0{\cdot}007$) agreed much more satisfactorily with the plotted observations.

The second series of observations, made with a greater amount of ether, showed the discrepancy from Dalton's gradually vanishing with increasing pressure.

It was also pointed out that in drawing his conclusions Regnault had not taken account of the supersaturation of air which would result from compressing air at constant temperature in the absence of nuclei for condensation, and the time that would be required under these circumstances for the gradual deposition of the excess of moisture upon the liquid surface exposed to it.

Moreover, it seems most unlikely that if the presence of air caused a discrepancy of 10 m.m. for a total pressure of 1000 m.m., the increase of the air pressure to 1400 m.m. should do away with the discrepancy previously caused. In other words, the line connecting the observations and intersecting the theoretical Dalton's law line at the highest pressure recorded is antecedently improbable and unreal.

It may therefore be concluded that Regnault's explanation is probably an unreal one, and that an actual divergence from Dalton's law is indicated. The amount of the divergence, however, cannot be finally deduced from the records of Regnault's observations, and must await a repetition of those or similar experiments in which the errors which may be due to supersaturation are guarded against.

Appointment.—Mr. W. Lincolne Sutton has been appointed Public Analyst for East and West Suffolk, Ipswich, and Bury St. Edmunds, in succession to the late Mr. J. Napier.

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* A Paper read before the British Association (Section A), Bristol Meeting, 1898.

THE ACTION OF LIVING STRUCTURES ON THE PHOTOGRAPHIC PLATE.*

By PERCY FRANKLAND, Ph.D., F.R.S.

The action exerted by uranium and its compounds, by zinc, and many metals, as well as by a number of organic substances, on photographic plates which has been revealed by the investigations of Becquerel, Colson, and especially of Russell, naturally leads to the enquiry as to whether *living* structures may not also be endowed with the power of recording their presence on the sensitive film of the photographer.

In commencing the study of this subject it has occurred to me that the group of the bacteria are perhaps of all organisms the best adapted for experiment in this direction, and I should like to take this opportunity of making known some of the preliminary observations which I have made.

Experiments A.

Gelatin dish cultivations of the well-known bacteria *Proteus vulgaris* and the *Bacillus coli communis* were used, the colonies being in each case densely packed. A sensitive plate (Imperial Flash-light) was placed on the top of the open dish, sensitive side towards the cultivation, another sensitive plate being placed beneath the dish containing the cultivation. Sensitive plates were similarly disposed above and below a similar dish containing the sterile gelatin culture medium. All the dishes and plates thus arranged were kept in a tin box in the dark room from June 11th to 20th, 1898, when they were developed with Imperial Standard Developer, and gave rise to the following effects:—

Proteus vulgaris	Top plate	Strong light effect.
	Bottom plate	No light effect.
B. coli communis	Top plate	Very strong light effect.
	Bottom plate	No light effect.
Blank gelatin dish	Top plate	No light effect.
	Bottom plate	No light effect.

The above results show that the bacterial cultures in question are capable of exerting an influence on the photographic plate at a distance of about half an inch, that this influence does not penetrate glass, and that the sterile gelatin medium does not affect the photographic plate.

The gelatin had only been inoculated with the bacteria in question on June 10th, so that the whole of the growth took place in the dark. The *Proteus vulgaris* liquefies the gelatin in about twenty-four hours, so that during the greater part of the nine days' exposure the medium must have been liquid. The *B. coli communis*, of course, does not liquefy gelatin.

Experiments B.

In the next instance I tried whether definite pictures of bacterial colonies could be obtained by placing the sensitive film in direct contact with the growths. For this purpose Austin Edwards's double instantaneous Frena films were employed, and cut so that they could be dropped sensitive side downwards into the dish containing the culture.

This was first done with a gelatin dish containing two large colonies which had grown from bacteria which had accidentally gained access from the air.

The colonies had been growing from June 4 to 24, and the Frena film was exposed to their action from June 24 to 30, 1898. On then developing with Imperial Standard Developer, distinct images of the colonies made their appearance, and were of sufficient density to yield a feeble print.

Better results were obtained with a cultivation of the *B. coli communis* consisting of large colonies. The cultivation was started on June 22, 1898, and the sensitive film exposed to it from July 1 to 14, 1898. On developing, very distinct images of the colonies were obtained, and sufficiently dense to print fairly well.

An exactly similar experiment made with the typhoid bacillus yielded a feebler result.

Experiments C.

As is well known, the growths of some bacteria are luminous in the dark. An agar-agar culture of the *Photobacterium phosphorescens* exhibiting a number of phosphorescent colonies, which had been growing from July 7 to 19, 1898, was placed in contact with the sensitive film from July 19 to 28, 1898. On development, very strong images of the colonies were obtained, and of much greater density than in the case of the non-phosphorescent bacteria with which I had previously experimented.*

Experiments D.

Much thicker growths are generally obtained by what is known as "streak culture," and it was thought that with such streak cultures probably stronger effects on the photographic plate would be obtained. This anticipation was fully realised in the case of a streak culture of *Proteus vulgaris* on agar-agar which had been growing from July 7 to 19, and was placed in contact with the Frena film from July 19 to 28, 1898. This yielded a very strong picture on development.

These preliminary experiments enable the following conclusions to be drawn:—

1. That ordinary bacterial cultures on gelatin and agar-agar are capable of affecting the photographic film, even at a distance of half an inch, whilst, when placed in contact with the film, definite pictures of the bacterial growths can be obtained.
2. As this action does not take place through glass, it is in all probability due to the evolution of volatile chemical substances which enter into reaction with the sensitive film, and I think it will be found to be analogous to the phenomena observed by Dr. Russell in the case of some organic compounds.
3. As far as my experiments have gone, the action is exerted both by bacteria which liquefy (*Proteus vulgaris*) and which do not liquefy gelatin (*B. coli communis* and typhoid bacillus). It is, however, quite possible that considerable differences, as regards activity towards a photographic plate, may be found to exist in the case of different bacteria, and that this property may become of importance in their diagnosis.
4. Bacterial growths which are luminous in the dark (*e.g.*, *Photobacterium phosphorescens*) exert a much more powerful action on the photographic plate than the non-luminous bacteria with which I have hitherto experimented. In the case of these phosphorescent bacteria, the action on the photographic film is not perceptibly diminished by the interposition of a glass plate.

The experiments of which I have given some account are, of course, of an entirely preliminary character. Further experience will doubtless lead to improvement in the photographic effects obtained, and I propose extending these investigations, not only in connection with bacteria, but also in respect to other organised structures, vegetable and animal, living and dead.

I have pleasure in acknowledging the zealous help I have received in the photographic part of these experiments from my assistant, Dr. Turnbull.

Rhodin Patent.—The Appeal against Mr. Justice Bigham's judgment in the Castner Kellner action is likely to be reached by the end of next month, when the validity of the Rhodin Patent will again be fully considered.

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* A Paper read before the British Association (Section B), Bristol Meeting, 1898.

* I have since found that the influence of phosphorescent bacteria on the photographic film is capable of readily traversing glass.—October 1, 1898.

THE OXIDATION OF GLYCEROL IN PRESENCE OF FERROUS IRON.*

(Preliminary Notice).

By HENRY J. HORSTMAN FENTON, M.A.,
and
HENRY JACKSON, B.A., B.Sc.(Lond.).

It has previously been shown by one of the authors (*Trans. Chem. Soc.*, 1894; *B. A. Report* 1895, &c.) that the presence of a small quantity of *ferrous iron* exerts a specific influence on the oxidation of tartaric acid. One molecule of the acid loses two atoms of hydrogen, and the result is hydroxymaleic acid, $C_2(OH)_2(COOH)_2$. Hydrogen dioxide is the most efficient oxidising agent for the purpose, but a similar result may be brought about by atmospheric oxygen in presence of sunlight, or by chlorine, bromine, &c. The presence of ferrous iron is absolutely essential, but the proportion necessary bears little, if any, relation to the yield of the product.

Similar effects appear to be produced by certain other hydroxy-acids (*Proc. Chem. Soc.*, 1898, 119), and the results of these are under investigation.

Messrs. Cross, Bevan, and Claude Smith have subsequently undertaken the investigation of the behaviour of *carbohydrates* when oxidised under similar conditions, and some of their results have already been published (*Trans. Chem. Soc.*, 1898), and Dr. Morrell is making important observations in the same direction.

With the object of extending the investigation of this reaction to other classes of hydroxy-compounds, the present authors are engaged in a study of the behaviour of certain *polyhydric alcohols* when similarly treated with oxidising agents in presence of iron. The first of these substances which has been selected is *glycerol*, and in this case again the presence of ferrous iron is found to exert a remarkable influence, as will be evident from the following observations:—

When a solution of glycerol (1 mol.) is mixed gradually with strong (20 volume) hydrogen dioxide (1 mol.), at the ordinary temperature, little, if any, change takes place. No alteration of temperature occurs, and the mixture, even after it has stood for some days, gives very strong reactions of hydrogen dioxide. Fehling's solution, in the cold, is unaffecteed, and the addition of phenyl-hydrazine acetate merely gives rise to an evolution of gas, owing to the presence of hydrogen dioxide, with slight precipitation of resinous matter. But when an exactly parallel experiment is made with the previous addition of a very small quantity of ferrous sulphate, a very powerful action results. The peroxide is now consumed almost immediately and the liquid becomes hot—the temperature, in fact, rises nearly to the boiling-point if the peroxide is added quickly. The resulting solution now strongly reduces Fehling's solution in the cold, and, when mixed with phenyl-hydrazine acetate at the ordinary temperature, a bulky yellowish-brown precipitate begins to separate almost immediately, and continues to do so for several days.

The substance thus precipitated crystallises from hot benzene in beautiful transparent golden prisms, which melt at 130°—131° (uncorr.), and is found by analysis to have the composition $C_{15}H_{16}N_4O$. It is, in fact, identical with *glycerosazone*, which has been obtained by Fischer and Tafel from "glycerose," by Piloty and Ruff from dihydroxy-acetoxime, and by Piloty from dihydroxy-acetone.

The oxidation-product obtained in the manner above stated may therefore be dihydroxy-acetone, glyceraldehyde, or, like Fischer's "glycerose," a mixture of both.

This product is now being investigated, and the authors also intend to make similar experiments with erythritol, mannitol, and other polyhydric alcohols.

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* A Paper read before the British Association (Section B), Bristol Meeting, 1898.

THE ACTION OF CERTAIN SUBSTANCES ON THE UNDEVELOPED PHOTOGRAPHIC IMAGE.*

By C. H. BOTHAMLEY, F.I.C., F.C.S.

It has been known for some time to practical photographers that just as there are substances that, like printer's ink, produce developable images when allowed to remain in contact with photographic plates, so there are others that under similar conditions will destroy a developable image previously produced on a photographic plate by the action of light. The author described one case in which printers' ink, acting through three or four thicknesses of tissue paper, destroyed the image previously produced by light; and others, in which the image was partially destroyed by exhalations from the material forming the hinges of double dark slides in which the plate had been kept for some time after being exposed.

Abney showed, many years ago, that the developable image is destroyed by the action of a solution of hydrogen peroxide, and the author finds that this effect is produced by the vapour as well as by the liquid. It is well known that hydrogen peroxide is produced during the oxidation of many substances; and these two facts together suggested the conclusion that the destruction of the photographic image, in cases such as those described, is really due to hydrogen peroxide. It was found that the vapour of turpentine, and other substances that are known to yield relatively large quantities of hydrogen peroxide during their oxidation by air, are particularly active in destroying the developable image produced by light.

The results are exactly the opposite of those described by Russell, and the author confirms Russell's observation that hydrogen peroxide vapour itself is capable of producing a developable image in a short time. The facts indicate that when hydrogen peroxide or substances that produce hydrogen peroxide during their oxidation by air, act on photographic plates in small quantity, or for a short time, they produce a developable image; but when allowed to act in larger quantity, or for a much longer time, they produce the opposite effect, and destroy the image already produced by light. In some cases it was found that in the early stages of the reaction the reducing effect of the substance was added to the effect of light, but on prolonging the action both effects were destroyed.

The observations are being continued.

THE TEACHING OF SCIENCE IN ELEMENTARY SCHOOLS.†

The Committee are able to report that the quantity, if not the quality, of the teaching of science subjects in elementary schools has made progress during the past year. Table A, made up from the return issued by the Education Department, gives the figures for the scientific class subjects as compared with English. In the report for last year it was mentioned that the number of school departments taking object lessons would greatly increase, as the Government code of regulations announced that they would become obligatory in the three lower standards on and after September 1, 1896. We now see the result, so far as the schools are concerned whose school year ended between August 31, 1896, and August 31, 1897, but

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* Abstract of a Paper read before the British Association (Section B), Bristol Meeting, 1898.

† Report of the Committee, consisting of Dr. J. H. Gladstone (Chairman), Professor H. E. Armstrong (Secretary), Professor W. R. Dunstan, Mr. George Gladstone, Sir John Lubbock, Sir Philip Magnus, Sir H. E. Roscoe, and Professor S. P. Thompson. Read before the British Association (Section B), Bristol Meeting, 1898.

the full effect cannot appear until the next year's return, the whole of which will be within the obligatory period.

The number of departments in "schools for older scholars" for 1896-97 was 23,080, all but ten of which took one or more class subjects. But History was taken in 5133 departments, and needlework (as a class subject for girls) in 7397 departments, and sundry minor subjects in 1056, making, with the other four subjects of the table, a total of 55,456. This shows an average of more than 2½ class subjects to each department; but it must be borne in mind that the same subject is not always taken in all the standards, in which case three class subjects will appear in the return.

It was remarked in the last report that "the increased teaching of scientific specific subjects in the higher standards is the natural consequence of the greater attention paid to natural science in the lower part of the schools." Table B shows the correctness of this inference.

It appears that the mathematical subjects still command the most favour on the part of the teachers, Algebra having taken a very remarkable lead. All the physical sciences have increased even more than might have been expected from the increase of scholars. The Principles of Agriculture is the only subject that shows an actual decrease.

Estimating the number of scholars in Standards V., VI., and VII. at 615,000, the percentage of the number examined in these specific subjects, as compared with the number of children qualified to take them, is 26·6; but it should be remembered that many of the children take more than one subject for examination. The following table gives the percentage for each year since 1882, and shows that Science is gradually recovering from the great depression of about eight years ago:—

1882-83 ..	29·0 per cent	1890-91 ..	20·2 per cent
1883-84 ..	26·0 ,,	1891-92 ..	19·7 ,,
1884-85 ..	22 6 ,,	1892-93 ..	20·2 ,,
1885-86 ..	19·9 ,,	1893 94 ..	20·9 ,,
1886-87 ..	18·1 ,,	1894-95 ..	22·7 ,,
1887-88 ..	16·9 ,,	1895-96 ..	24·2 ,,
1888-89 ..	17·0 ,,	1896-97 ..	26 6 ,,
1889 90 ..	18·4 ,,		

The Returns of the Education Department here given refer to the whole of England and Wales, and are for the school years ending with August 31. The statistics of the London School Board are brought up to the year ending with Lady Day, 1898. They also illustrate the great advance that has been made in the teaching of Elementary Science as a class subject, and they give the number of children as well as the number of departments.

Years.	Departments.	Children.
1890-91	11	2,293
1891-92	113	26,674
1892-93	156	40,208
1893-94	183	49,367
1894-95	208	52,982
1895-96	246	62,494
1896-97	364	86,638
1897-98	322	70,626

The last year shows an apparent falling-off in the teaching of this subject, but, as has been mentioned above, the Government having made the giving of object lessons obligatory in the lower standards, 442 departments, with 75,993 children, have already adopted them. This has caused a reduction in the teaching of "Elementary Science" under that name; but, taking the two subjects together, this must be regarded as a very considerable gain.

The Education Department continues to meet the objection against the limitation under the Code by which only two class subjects are allowed to be taught, by adding combined courses of study. This year a new course of this character has been introduced into Schedule II., described as "Elementary Science and Geography Combined." And as, under the present regulations, one of the class subjects must be such as can be taught by means of object lessons in the lower standards, some such subject as the combined one above mentioned must be taken. A copy of the scheme is given in the Appendix, by which it will be seen that in the lower standards the phenomena of the land and water are to be illustrated experimentally as an introduction to Geographical Science.

A similar principle has been adopted in respect of the specific subjects. Hitherto Chemistry has formed a course of itself, and Physics has been divided into two separate courses, the one dealing with Sound, Light, and Heat, and the other with Magnetism and Electricity; but they formed only three out of the nineteen subjects from which choice could be made. A separate course of Elementary Physics and Chemistry combined has now been introduced, which is set out in the Appendix, and which is admirably adapted for experimental investigation at the hands of the students themselves.

The work under the Evening Continuation Schools Code continues to progress, as will be seen from Table C.

It is again evident that the mathematical subjects are rapidly increasing in favour, and that Agriculture is decreasing. It will be noticed with satisfaction that the Science of Common Things is receiving greatly increased attention, but it is a matter of regret that there is a decrease in the time given to Elementary Physiography, and still more so in the case of Elementary Physics and Chemistry. Agriculture would become a more valuable and probably a more popular subject of study if a really good practical course were devised.

An important change has been taking place in Scotland. The code of the Scotch Education Department now admits of the possibility of gaining the full class grant although only two subjects are taken. As one of these must be English, and in the higher standards provision must be made for history or geography or both, the teaching of Science as a class subject has been greatly reduced during the last two years. But a new article in the Code for 1895 offers a special grant of a shilling on the average attendance of boys who are satisfactorily taught "elementary science"; and this has far more than made up the deficiency. In fact the aggregate total of children learning elementary science in the Scotch schools has risen from 34,151 in 1894-95 to 85,671 and 133,855 respectively in the two succeeding years.

Your Committee have frequently referred to the anomaly that pupil teachers are not obliged to receive any instruction in Natural Science, although they may have to give instruction in such subjects, either specifically or in the form of object lessons; indeed, if they should be in charge of a class of the three lower standards it would be obligatory upon them to give such object lessons. A Departmental Committee, consisting of the Rev. T. W. Sharpe, Her Majesty's Chief Inspector of Schools, as Chairman, and several Inspectors and Principals of Training Colleges and Pupil-teacher Centres, have reported upon the pupil-teacher system. They recommend that the age for entering as pupil teachers should be raised, and that the interval between the elementary school and their apprenticeship should be passed at a secondary school. This would by no means ensure that the young people would receive any instruction in Science during that period of their career. No alteration is proposed in the optional Science Course prescribed by the Code of the Education Department, except that the Queen's Scholarship examination is to be limited to the elementary stage of Physiography prescribed in the syllabus of the Science and Art Department. With regard to the College Course the recommendation is singularly weak, Science being placed as an optional subject, without any definite course of study prescribed. For the first two years it is laid down that of the optional subjects not more than two must be taken out of a list of four or six respectively, some of which from their very nature are almost sure to be taken in preference.

TABLE A.

Class subjects—Departments.	1890-91.	1891-92.	1892-93.	1893-94.	1894-95.	1895-96.	1896-97.
English	19,825	18,175	17,394	17,032	16,280	15,327	14,286
Geography..	12,806	13,485	14,256	15,250	15,702	16,171	16,646
Elementary Science	173	788	1,073	1,215	1,712	2,237	2,617
Object Lessons	—	—	—	—	—	1,079	8,321

TABLE B.

Specific subjects—Children.	1891-92.	1892-93.	1893-94.	1894-95.	1895-96.	1896-97.
Algebra	28,542	31,487	33,612	38,237	41,846	47,225
Euclid..	927	1,279	1,399	1,468	1,584	2,059
Mensuration	2,802	3,762	4,018	5,614	6,859	8,619
Mechanics	18,000	20,023	21,532	23,806	24,956	26,110
Animal Physiology	13,622	14,060	15,271	17,003	18,284	19,989
Botany	1,845	1,968	2,052	2,483	2,996	3,377
Principles of Agriculture	1,085	909	1,231	1,196	1,059	825
Chemistry	1,935	2,387	3,043	3,850	4,822	5,545
Sound, Light, and Heat	1,163	1,168	1,175	914	937	1,040
Magnetism and Electricity	2,338	2,181	3,040	3,198	3,168	3,431
Domestic Economy	26,447	29,210	32,922	36,239	39,794	45,869
Total..	98,706	108,434	119,295	134,008	146,305	164,089

TABLE C.

Science subjects.	Units for payment.							
	England and Wales.				London School Board.			
	1893-4.	1894-5.	1895-6.	1896-7.	1893-4.	1894-5.	1895-6.	1896-7.
Euclid	595	1,086	1,648	2,270	10	29	7	—
Algebra	3,940	6,657	10,374	14,260	316	302	535	714
Mensuration	14,521	32,931	41,772	50,748	279	374	452	369
Elementary Physiography	2,554	4,045	6,590	6 325	37	9	5	—
Elementary Physics and Chemistry ..	6,500	7,850	6 749	5,183	79	200	152	129
Science of Common Things	6,223	10,350	12,906	18,293	231	262	468	556
Chemistry	3,484	7,814	8,222	9,641	212	455	404	488
Mechanics	841	1,148	1,458	2,196	230	197	209	127
Sound, Light, and Heat	500	1,046	861	1,156	—	15	11	7
Magnetism and Electricity	2,359	4,451	5,073	6,990	662	776	783	939
Human Physiology	5,695	8,395	7,825	10,047	91	68	56	49
Botany	336	547	905	1,080	5	91	97	32
Agriculture	3,579	4,991	4,694	4,061	—	—	—	—
Horticulture	438	1,140	1,812	1,911	—	—	—	—
Navigation	42	69	142	99	—	—	—	—
Totals..	51,607	92,520	111,031	134,260	2,152	2,778	3,179	3 410

An important letter has been addressed to the Right Hon. Sir John Gorst by Sir Philip Magnus, the Chairman of the Joint Scholarship Board, in conjunction with the Chairman of its four educational committees. They point out the necessity of securing the proper training of those who will be teachers of scientific subjects, and that the instruction of pupil teachers in Science is now often carried on, under great pressure, by a system of cram, and even by persons who have not themselves any satisfactory knowledge of modern scientific methods. They suggest as a remedy that the first part only of the elementary stage, Physiography, be compulsory; that the teaching of this subject be recognised only where it is given with proper accessories, all pupils performing the experiments in a series of at least twenty-four lessons of two hours' duration; and that inspectors should be required particularly to report whether proper apparatus and accessories are provided.

In last year's report the Committee referred to what Mr. Heller was doing in respect of the teaching of Science in the schools of the London School Board. He has since obtained a better appointment at Birmingham, but the syllabus of lessons which he prepared is still employed in the schools. This of course requires that the masters and mistresses should be qualified for carrying it out, and for this purpose classes of twenty-four hours are conducted for their benefit by the Science Demonstrators. These gentlemen have lately agreed upon two separate syllabuses for masters and mistresses, which follow in general the scheme they are expected to teach to their scholars. The classes of a similar kind that have been carried on hitherto have been appreciated by the teachers, and the Board are increasing their laboratory and other accommodation for the purpose. It is recognised that it will be necessary to continue these teachers' courses for some years, in order to overcome the difficulty which now exists in consequence of the general want of practical experiment in such instruction in Science as has been given in the course of training of most class teachers.

APPENDIX.

Schedule II. — *Course D. Elementary Science and Geography Combined.*

Standards I., II., *and* III.—Annual courses of about thirty object lessons, of which elementary geography should form a part, beginning with the simplest phenomena which the children can observe:—Land, water, the form of the earth, the sea, hills, valleys, rivers, proceeding to notions of locality and distance, and the means of representing all of these by modelling in sand or other material, and by a map, with special reference to the map of England.

The other object lessons should include some of the various subjects suggested in this Schedule under the head of Elementary Science.

Standard IV. — Geography of England, physical and political.

Lessons on animals and on materials used in agriculture, or in some simple manufactures.

Standard V.—Geography of the British Isles, with some knowledge of India and one or more of the Colonies.

Lessons on means of locomotion, and on processes used in agriculture or manufacture.

Standard VI.—Geography of Europe, physical, political, and commercial.

Lessons on the physical laws that determine climate, animal life, locality of certain industries, &c.

Standard VII.—The work of the preceding years, with special knowledge of the British Empire, and of those portions of the world with which we are engaged in commerce.

Distribution of the races of mankind.

Schedule IV.—*Specific Subjects.* (13.) *Elementary Physics and Chemistry.*

1st stage.—Properties of common stuffs; relative density of solids and liquids; flotation of solids. The barometer and thermometer; their use; graphic representation of daily readings. Solution: water as a solvent; solubility of metals, &c., in acids; crystallisation of salt, soda, alum.

2nd stage.—Evaporation and distillation; heat absorbed in fusion of ice and in conversion of water into steam; density of ice; change in density of water on heating; moisture in air; wet and dry bulb thermometer. Study of iron rusting, and of combustion of candle, gas, oil, phosphorus; effect on metals of heating in air; discovery of active constituent of air.

3rd stage.—Chalk and lime; the burning of chalk or limestone; action of muriatic acid on chalk or limestone; carbonic acid; re-formation of chalk. Discovery of carbonic acid in air; its formation by combustion of carbonaceous materials and in respiration. Study of action of muriatic and vitriolic acids on zinc; combustion of the gas obtained, and discovery of the composition of water. Presence of air and solids dissolved in water; sea water; hardness of water.

THE CYANOMETRIC ESTIMATION OF SOME METALS.

By HARRY BREARLEY and HORACE JERVIS.

(Concluded from p. 179).

Manganese.—This element is precipitated when an insufficient amount of ammonium chloride is present, and, as the precipitation takes place very slowly, it is impossible to take full advantage of the delicacy of the indicator even by repeated filtrations. Such approximations as we were able to make under these circumstances showed that the precipitated manganese oxides did not interfere in any other way. If ammonium chloride be added to keep the manganese in solution there is no interference at all. The manganese may also be precipitated from the solution by using ammonium carbonate instead of ammonia. The manganous carbonate becomes bath coloured and less bulky in form after adding the cyanide, and may then be very readily filtered off. Where the filtration is easy and the precipitate not bulky an aliquot portion need not be filtered off; the nearly finished solution may be repassed through the filter, as is mentioned under zinc.

The harmlessness of manganese should be emphasised, because it has been repeatedly said to render this process of estimating nickel valueless.

Chromium.—The interference of this element cannot be avoided by the use of tartaric acid. The direct titration, in which cyanide is added until the AgI vanishes, cannot be reliably performed, because the indicator disappears long before it should, and the turbidities re-formed with silver nitrate so as to complete the reaction become more and more dense on standing. The reaction between the nickel and the potassium cyanide seems to be retarded by the joint presence of the tartrate and the chrome oxide salts, so it happens that if an excess of cyanide be added the results are the more approximately accurate, as a longer time is allowed to elapse before going back with the silver nitrate; and it may properly be imagined that by adding enough cyanide to quickly complete the reaction, as in the case of the copper titration, and then allowing to stand a while, very approximately accurate results might be obtained. Such a procedure, however, would require some knowledge of the amount of nickel present, and with such information to hand the acid titration may be quite as expeditiously and more accurately employed.

The mixed solution of chromium and nickel salts indicates itself by a change in colour from greenish-blue to full green when the solution is neutralised; the blue tint is recovered by a drop of HCl, and the titration proceeded with. It sometimes happens, particularly when the cyanide contains considerable amounts of carbonates, that a precipitate begins to form before all the cyanide is added. We have not found small precipitates thus formed to interfere. Test analyses for acid titration:—

0·05 0·10 gr. Cr present.
0·1000 0·0999 gr. nickel recovered.

Table I. shows that the interference may also be avoided by converting chromic oxide salts into chromic acid salts. In this case it is only necessary to remark that a reaction between the alkaline chromate and the ammoniacal solution of nickel may precipitate a basic chromate of nickel. This may be obviated by adding ammonium sulphate to the mixture before making alkaline.

Tin.—In the presence of stannous salts a red colouration is produced on adding the cyanide—probably due to the subcyanide of nickel investigated by Moore (Chemical News, lxviii., 295; lxxi., 81). This complication should be avoided by oxidising the stannous to stannic salts, in the presence of which perfectly accurate estimations may be made.

Molybdenum (*Soda Molybdate*).—The results may be falsified by the fact that in an ammoniacal solution the nickel is precipitated by the molybdate in a form which is not readily acted upon by the potassium cyanide. This nickel-molybdenum precipitate forms only very slowly, and is still further retarded by the presence of ammonium sulphate. If the titration is not unduly delayed after making the solution alkaline, the results are perfectly accurate.

Arsenic (*Soda Arsenite*).—The larger amounts of this compound cause the results to be somewhat low. The error is always less than 1 per cent, but it is so persistently a negative quantity that it cannot be well accounted for by experimental error. After converting into arsenate by making slightly acid with nitric acid, adding a little bromine water, boiling off excess, and titrating as usual, we find the results to be perfectly accurate. As with molybdenum, there should be no unnecessary delay between making alkaline and adding the cyanide.

Antimony and Bismuth.—The oxychlorides formed on diluting do not interfere. Their precipitation can be prevented by previously adding a small amount of tartaric acid, after which the direct titration may be accurately employed.

Lead (*Acetate*).—Even when sulphates or chlorides happen to be precipitated, lead does not interfere with the accuracy of the nickel estimation. The precipitates may be obviated by using nitrates instead of sulphates to heighten the iodide turbidity.

Uranium (*Uranyl Nitrate*).—Ammonia throws down a yellow precipitate which soon clogs the filter. It is best to use the carbonate of ammonium, an excess of which re-dissolves the yellow precipitate.

Tungsten (*Soda Tungstate*).—No interference, or other visible indication that any foreign metal is present.

Citric Acid.—This reagent is not nearly so satisfactory as tartaric acid for preventing the formation of precipitates in alkaline solutions. It causes the results to be low.

The Acid Titration.

It is, theoretically, valid to object that potassium cyanide and the double cyanide of nickel and of copper are decomposed in an acid solution. There seems to be no difficulty in always providing a neutral solution from which one may attain any degree of acidity desirable. We prefer to work with a very *slightly* acid solution; but to meet the above objection, and because it is desirable to know the limit of accuracy, the stability of a procedure as it were, we have made some experiments on this point.

To a solution measuring 200 c.c., and containing rather more cyanide than is needed to combine with 0·1 grm. nickel, there was added 10 c.c. HCl (two normal strength), and the whole allowed to stand three or four minutes. On estimating the cyanide the results were always within 0·3 per cent of the truth. In the same way the double cyanides $Ni(CN)_2 \cdot 2KCN$ and $Cu(CN)_2 \cdot 2KCN$ were formed in an alkaline solution. This solution was then made acid, and, like the previous test, allowed to stand. The error with the nickel compound was within 0·2 per cent, and with the copper compound (HCN could be faintly smelled) the worst result was only 0·6 per cent out. It is worthy of remark that while the nickel solution remained clear throughout, a white precipitate was thrown down from the copper solution, which on standing clotted somewhat, and was not then *immediately* re-dissolved on making alkaline again.

This (acid) form of titrating a solution was incidentally applied to eliminate the influence of manganese on the cyanometric estimation of copper (Chem. News, lxxvi., 303). It was there related as a chance observation which had happily overcome a difficulty; its use in the foregoing cases, however, shows it to be so widely applicable as to deserve some consideration.

Already the procedure has eliminated the error from the cyanometric estimation of nickel in presence of chromium, iron, zinc, and aluminium, and from the estimation of copper in presence of manganese. An obvious enquiry is whether the interference of chromium, iron, &c., with the estimation of copper can be avoided in the same way. At present this question must be answered negatively. The enormous error which chromium introduces can in this way be reduced about twenty times, but it has not been altogether eliminated. We are still considering this point.

Taken altogether, the amended results suggest that the interference of chromium, aluminium, and iron, when the estimation of Ni or Cu is performed in the usual way, are due in each case to the carrying down of part of the nickel or copper by the more or less compact precipitates which are formed in an alkaline solution by the interfering elements. It is easy to understand, however the nickel or copper may be associated with the precipitate, that the cyanide can react less readily with the precipitated portions than with the portions remaining in solution—hence the invariable negative value of the interference.[*]

The proof of this view would require us to show that on making alkaline, part of the copper or nickel is precipitated along with the interfering element, if such were not already well known to be the case. However, the point was submitted to experiment, and, as the results were obtained under comparative conditions, they are interesting.

Each test contained 0·1 grm. Ni, 0·1 grm. of the interfering metals, and an excess of 10 c.c. 2N. ammonia in a volume of 250 c.c. The nickel was estimated in a filtered fraction.

Interfering Metal.	Ni in solution.
Chromium	0·0041
Aluminium	0·0182
Iron	0·0358.

These separations were made under just such conditions as obtained when the corresponding interferences of Table I. were being determined, and it is noteworthy that chromium which carries down most of the nickel interferes most with the cyanometric estimation of nickel, and that aluminium and iron in each case are in the same order,[*]

We may then reasonably conclude that the acid titration gives improved results, because the double cyanides $Ni(CN)_2 \cdot 2KCN$ and $Cu(CN)_2 \cdot 2KCN$ are formed before the interfering metal is precipitated, and hence the reaction illustrated by the above table is avoided.

If the interference of a precipitable element were obviated by these means, one might not safely conclude that the carrying down caused the error, but they might suspect such to be the case. Such a case is presented by the behaviour of manganese in the cyanometric estimation of copper. From the frequent association of copper and manganese and the extensive use made of the estimation of copper by KCN, this interference has been the subject of much speculation. The issue is somewhat complicated by the fact that the precipitate ($Mn(HO)_2$) also exerts a reducing action. This latter consideration led Field to explain the results by the formation of a colourless compound of the two metals, and it has been remarked later Chemical News, lxxvi., 303) that Field's suggestion is theoretically valid. The lack of opportunity compels us to reserve this point for further investigation.

Totley, near Sheffield, September 3, 1898.

ON THE

TRANSFORMATION OF CHEMICAL ENERGY INTO ELECTRIC ENERGY.[†]

By Prof. F. FOERSTER.

(Continued from p. 182).

The solution of this problem from the commercial point of view encounters two great difficulties. On the one hand, the gas cannot react except when it is in contact with the electrodes and the electrolyte. On the other hand, it is necessary to use very large quantities of gas in very little time, to obtain any considerable amount of electric current. These two questions were recognised by the first chemists who engaged themselves with the problem, when they were endeavouring more to apply the Grove cell commercially than to make carbon cells. Westphal in 1882 saw these difficulties, and in his patent (German patent, No. 22,393) described a number of methods which allowed more particularly an intimate and continuous contact of the gas with the electrodes and the electrolyte. For example, he made the gas pass through porous carbon electrodes, and he also introduced it under the electrolyte by means of slightly inclined tubes open at the lower end, &c. It suffices to mention these pro-

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[*] Zinc must be taken as an exception, as it can itself react with the cyanide.

[*] H. von Jüptner (*Stahl und Eisen*, xiv., 872; *Journ. Iron and Steel Inst.*, 1894, i., 616; ii., 425) calls attention to the fact that Fresenius recommends ammonia for separating small quantities of iron from nickel. Von Jüptner further finds that the process is applicable when the iron is 200 times the weight of the nickel present, and hence may be used in the analysis of steels. Where the steel also contains several percents of chromium, as is occasionally the case, one needs to be reassured of the sufficiency of Jüptner's proposal.

[†] *Moniteur Scientifique*, Series 4, vol. xii., July, 1898.

posals, as they have not been commercially successful. They do, however, give useful hints to the future worker on the subject. In the same way, the lack of practicable application compels us to pass by Scharf's cell, in which dilute sulphuric acid is used, with carbon electrodes, and in which the electric current is looked for by the combustion, in the cold, of hydrogen, or of hydro-carbides.

We shall, however, examine the Mond and Langer element much more closely (*Zeit. f. Elect.*, iv., p. 139). The first problem presented to these chemists was to accelerate the reaction of the gases, and to achieve this end they made use of a method well known in laboratories —viz., platinum black. We well know that the accelerating action of this substance is based on the facility it possesses of condensing the gases on its surface. But, on the other hand, MM. Mond and Langer found that the action of platinum black is weakened by contact with liquids, which forced them to follow, in the construction of their batteries, the principles of the dry battery where the electrolyte is imbedded in porous materials.

For porous materials we can make use of plaster, asbestos, cardboard, &c., which are soaked in the electrolyte and then enveloped in perforated sheets of platinum, or of gold covered with a layer of platinum black. Care must be taken to make the surface of contact between the gas and the platinum black as great as possible. These plates are then connected in such a manner that their surfaces covered with platinum form the greater poles of the cells of which the other pole is composed of two insulated plates. To start the battery we have only to let air enter one-half of the cells, alternatively with hydrogen or hydrocarbides in the other half.

By using hydrogen. Mond and Langer succeeded in transforming 50 per cent of the heat of combustion into electric energy. The cell with an active surface of 700 square centimetres (0·35 grm. of platinum and 1 grm. of platinum black) gave them a current of 2 to 2·5 ampères and 0·73 volt. The principal fault of this apparatus is the uncertainty of its return; the absorption of the gas by the platinum black is very variable and cannot be controlled, and, further, the re-partition of the electrolyte in the porous substance is also subject to variations; and, finally, the construction of the apparatus is rather expensive.

If, in the Mond and Langer cell, the hydrogen is replaced by hydrocarbides, its electromotive force becomes at first much greater; but it falls after a few days, and then remains very low. As was pointed out by Quincke (*Zeit. f. Electr.*, iv., p. 52) this phenomenon may be attributed to the transformation of the hydrocarbides into complicated carbonised acids.

The idea of accelerating the action of the gas by using catalytic materials is of enormous importance in the construction of gas cells, above all when the hydrocarbides, the carbonic oxide, &c., such as they are obtained commercially, as well as the oxygen of the air, are diluted with large quantities of nitrogen. Zettel (*Zeit. f. Elect.*, ii., p. 543), has recently, in the Ostwald laboratory, made some experiments in this direction, for the purpose of finding catalytic materials which would accelerate oxidation. His work, however, has not been successful, but he was able to note one interesting phenomenon: his cell—which consisted of a sheet of platinum covered with platinum black, plunged partly into weak sulphuric acid, and connected with a copper plate—showed a very sudden decrease of electromotive force, as soon as the current exceeded a certain limit. This phenomenon may be explained by taking note of the fact that the absorbing power of the platinum black for the gas is limited, and that in this case the oxygen only acts in the condensed state; the effective action of the cell should therefore diminish when the oxygen is consumed more quickly than it can be absorbed by the platinum.

Further, this experiment shows that platinised platinum, besides its high price, has the disadvantage of only acting very slowly.

In the year 1894, Borchers, working on an idea of Ostwald's, proposed an altogether model method for the construction of a carbon element. He first endeavoured to find an electrolyte which could keep carbonic oxide and the hydrocarbides in solution. Under this heading chloride of the protoxide of copper, in either commercial or acid solution, presents, as we know in gas analysis, great advantages.

A glass cell, divided into three compartments by perforated partitions, so as to allow free communication throughout, was filled with a solution of cupreous chloride. In the two outside compartments, carbonic oxide or coal-gas was introduced by means of copper tubes; the middle compartment contained a carbon cell, by which air was introduced. Borchers was enabled to get an electromotive force of 0·4 volt through a resistance of 50 ohms.

However, it was soon noticed that this cell produced electrical energy without forming carbonic acid, from which it was concluded that here the electric energy was produced, not by the combustion of the gas, but by other reactions, among which the most important would be the solution of the copper tube in the chloride.

(To be continued).

THE
ACTION OF LIGHT UPON DYED COLOURS.[*]

(Continued from p. 177).

Class III.—Moderately Fast Colours. (Wool).

The colours of this class show distinct fading at the end of the second period (August 22 to September 29, 1896), which becomes more pronounced at the end of the third period (September 29 to November 5, 1896). A pale tint remains at the end of the fourth "period of exposure" November 5, 1896, to May 22, 1897), and at the end of a year's exposure the colour has entirely faded, or at most only traces of colour remain.

Azo Colours.

Wool Book XII.

Acid Colours.—

*3. Azo Acid Brown. Constitution not published.
6. Fast Brown. From xylidine-mono-sulphonic acid and α-naphthol. S. and J. II. 80.
12. Fast Brown. From naphthionic acid and resorcinol. S. and J. III. 164.
14. Diamond Brown. Constitution not published.

Direct Cotton Colours.—

7. Congo Brown G. From sulphanilic acid and benzidine, with resorcinol and salicylic acid. S. and J. III. 269.
9. Thiazine Brown G. Constitution not published.
12. Congo Brown R. From α-naphthylamine-sulphonic acid L and benzidine, with resorcinol and salicylic acid. S. and J. III. 270.
14. Hessian Brown 2BN. Constitution not published.
16. Hessian Brown 2B. From sulphanilic acid and benzidine with resorcinol. S. and J. III. 277.
17. Thiazine Brown R. Constitution not published.
20. Diamine Bronze G. From benzidine, with salicylic acid and amido-naphthol-disulphonic-acid-H-azo-*m*-phenylene-diamine. S. and J. III. 263.
41. Diamine Brown M. From benzidine with salicylic acid and γ-amido-naphthol-sulphonic acid.
43. Diamine Brown B From benzidine, with phenyl-γ-amido-naphthol-sulphonic acid.
45. Benzo Dark Brown. Constitution not published.

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[*] Report of Committee, consisting of Dr. T. E. Thorpe (Chairman), Professor J. J. Hummel (Secretary), Dr. W. H. Perkin, Professor W. J. Russell, Captain Abney, Professor W. Stroud, and Professor R. Meldola. (Drawn up by the Secretary). Read before the British Association (Section B), Bristol Meeting, 1898.

Direct Cotton Colours Developed.—
*1. Diamine Cutch. Constitution not published. Naphthylene Violet azotised and developed with sodium carbonate. S. and J. III. 256.

Azoxy Colours.

Direct Cotton Colours.—
22. Mikado Brown 2B. Constitution not published.
23. Mikado Brown G. Constitution not published.
24. Mikado Brown B. Constitution not published.

Natural Colouring Matters.

Wool Book XIII.
Mordant Colours.—
*Ventilago (Cu) (Fe). Ventilago madraspatana (root-bark).
Sanderswood (Cu) (Fe). Pterocarpus santalinus (wood).
Barwood (Cu) (Fe). Baphia nitida (wood).
Camwood (Cu) (Fe).

NOTES.—Diamine Brown M loses its reddish hue and becomes apparently darker during the first "fading period"; the altered colour fades slowly, and finally leaves at the end of the year a pale drab colour. Azo Acid Brown acquires a more yellowish hue during the first "fading period"; the colour then fades very gradually without further change of hue, leaving at the end of a year a very pale brown. It might fairly well be classed as a "fast colour." The Mikado Browns are by no means so fast to light as the Mikado Oranges and Yellows; they experience the greatest change in depth of colour during the first "fading period"; the altered colour, which is yellower than the original one, then fades very gradually, and leaves at the end of the year a fairly good buff colour.

CLASS IV.—FAST COLOURS. (WOOL).

The colours of this class show comparatively little fading during the first, second, and third periods. At the end of the fourth "period of exposure" a pale shade remains, which at the end of the year's exposure still leaves a pale shade.

Azo Colours.

Wool Book XII.
Direct Cotton Colours.—
5. Toluylene Brown G. From toluylene-diamine-sulphonic acid and *m*-phenylene-diamine. S. and J. III. 241.
6. Direct Cotton Brown R. From amido-nitroso-stilbene-disulphonic acid and aniline.

Natural Colouring Matters.

Wool Book XIII.
Mordant Colours.—
12. Cochineal (Cr). Coccus cacti (insect).

CLASS V.—VERY FAST COLOURS. (WOOL).

The colours of this class show a very gradual fading during the different periods, and even after a year's exposure a moderately good colour remains.

Oxyketone Colours.

Wool Book XIII.
Mordant Colours.—
Alizarin Bordeaux B (Cr) (Cu). Tetra-oxy-anthraquinone (1.2.5.8). Quinalizarin. S. and J. III. 403.
Alizarin Bordeaux G (Cr) (Cu).
Alizarin Bordeaux GG (Cr) (Cu).
Alizarin Maroon (Cr) (Cu). Amido purpurin. S. and J. III. 394.
Alizarin Brown (Cr) (Fe). Diamido-alizarin.
Anthracene Brown (Cr) (Fe). Tri-oxy-anthraquinone (1.2.3) Anthragallol. S. and J. III. 396.

Natural Colouring Matters.

Wool Book XIII.
Mordant Colours.—
Morinda Root (Cr) (Cu) (Fe). Morinda citrifolia (root).
Mang-kudu (Cr) (Cu) (Fe). Morinda umbellata (root-bark).
Chay Root (Cr) (Cu) (Fe). Oldenlandia umbellata (root).
Munjeet (Cr) (Cu) (Fe). Rubia cordifolia (root).
Madder (Cr) (Cu) (Fe). Rubia tinctorum (root).
Lac-dye (Cr) (Cu) (Fe). Coccus ilicis (insect).
Cochineal (Cu) (Fe). Coccus cacti (insect).

Additional Colours.

Oxidation Colour.—
Chromogen I. (1.8) Dioxy-naphthalene-(3.6)-disulphonic acid; oxidised with bichromate of potash. S. and J. III. 504.

(To be continued).

A TABLE OF ATOMIC WEIGHTS.*

By THEODORE WILLIAM RICHARDS.

(Concluded from p. 183).

AN important deviation from the usually accepted figures is to be seen in the value assigned to platinum below. Our knowledge of the atomic weight of this element depends chiefly upon the elaborate and carefully executed work of Seubert (*Ber. d. Chem. Ges.*, 1881, xiv., 865) and Halberstadt (*Ibid.*, 1884, xvii., 2962), and the only question is how this is to be interpreted. These chemists studied the platinchlorides and platinbromides of potassium and the platinchloride of ammonium, weighing these compounds and some of the products of their decomposition. The careful study of the results shows at once that some source of error lies hidden in all the data, for the various ratios are not wholly consistent, even in any one series. Any value from 194·7 to 196·0 may be obtained from the figures (Clarke, "Re-calculation," 1897, p. 334), the results of Seubert's work being the least discordant among themselves. Dittmar and McArthur (*Trans. Roy. Soc. Edinburgh*, 1887, xxxiii., Part II., 561) explain the discrepancy in the case of potassic platinchloride by assuming that the complex salt contains traces of hydroxyl replacing the halogen and traces of hydrogen replacing the potassium, as well as a small amount of extra occluded potassic chloride. They adduce experimental evidence in proof of this view, but Seubert showed in his reply (*Ber. d. Chem. Ges.*, xxi., 2179) that their hypotheses can hardly be applied to his determinations. Most of Seubert's and Halberstadt's inconsistencies may be explained by the supposition that the complex salts, like all substances crystallised from aqueous solution, contain certain traces of mother-liquor held in minute cells within the crystal structure, and that these traces of water are not free until the substance is disintegrated. I have accumulated a large amount of experimental evidence, soon to be published, upon this subject. Water is one of the most dangerous, although one of the least heeded, impurities in this kind of work; and in my opinion it is responsible for the lack of agreement in this case. Hence the best data for the calculation of the atomic weight of platinum seem to be those concerning the relation of the metallic platinum to the potassic chloride or potassic bromide formed by the decomposition of the complex salts, for the water must surely have been expelled from these products of the ignition. According to Clarke ("Re-calculation," page 333) potassic platin-

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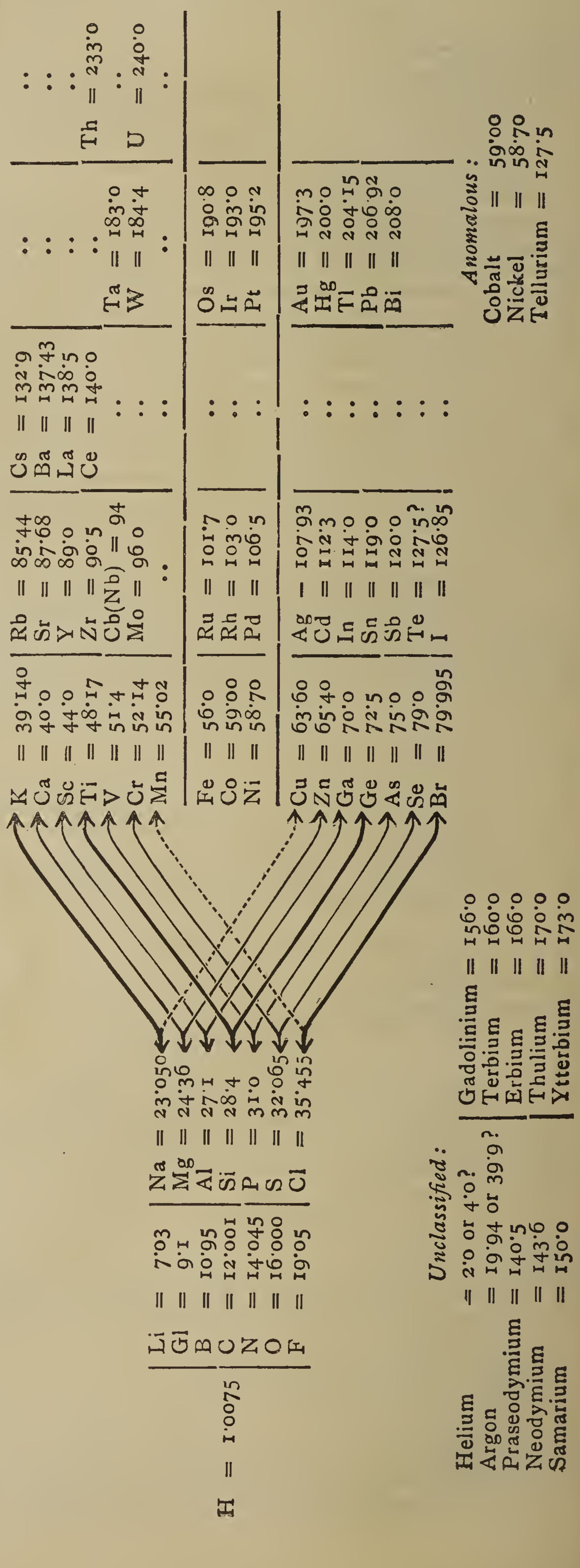
* Presented to the American Academy of Arts and Sciences, March 9, 1898. From the *American Chemical Journal*, xx., No. 7.

A TABLE OF ATOMIC WEIGHTS
OF SEVENTY-FOUR ELEMENTS.

Compiled in March, 1898, from the Most Recent Data.

Name.	Symbol.	Atomic weight.
Aluminium	Al	27·1
Antimony	Sb	120·0
Argon	A	39·9 ?
Arsenic	As	75·0
Barium	Ba	137·43
Beryllium	Be = Gl	9·1
Bismuth	Bi	208·0
Boron	B	10·95
Bromine	Br	79·955
Cadmium	Cd	112·3
Cæsium	Cs	132·9
Calcium	Ca	40·0
Carbon	C	12·001
Cerium	Ce	140·0
Chlorine	Cl	35·455
Chromium	Cr	52·14
Cobalt	Co	59·00
Columbium	Cb = Nb	94·0
Copper	Cu	63·60
"Didymium"	Nd + Pr	142 ±
Erbium	Er	166·0
Fluorine	F	19·05
Gadolinium	Gd	156·0 ?
Gallium	Ga	70·0
Germanium	Ge	72·5
Glucinum	Gl = Be	9·1
Gold	Au	197·3
Helium	He	4·0 ?
Hydrogen	H	1·0075
Indium	In	114·0
Iodine	I	126·85
Iridium	Ir	193·0
Iron	Fe	56·0
Lanthanum	La	138·5
Lead	Pb	206·92
Lithium	Li	7·03
Magnesium	Mg	24·36
Manganese	Mn	55·02
Mercury	Hg	200·0
Molybdenum	Mo	96·0
Neodymium	Nd	143·6
Nickel	Ni	58·70
Niobium	Nb = Cb	94·0
Nitrogen	N	14·045
Osmium	Os	190·8
Oxygen (standard)	O	16·000
Palladium	Pd	106·5
Phosphorus	P	31·0
Platinum	Pt	195·2
Potassium	K	39·140
Praseodymium	Pr	140·5
Rhodium	Rh	103·0
Rubidium	Rb	85·44
Ruthenium	Ru	101·7
Samarium	Sm	150·0
Scandium	Sc	44·0
Selenium	Se	79·0
Silicon	Si	28·4
Silver	Ag	107·93
Sodium	Na	23·050
Strontium	Sr	87·68
Sulphur	S	32·065
Tantalum	Ta	183·0
Tellurium	Te	127·5
Terbium	Tb	160·0
Thallium	Tl	204·15
Thorium	Th	233·0
Thulium	Tu	170·0 ?
Tin	Sn	119·0
Titanium	Ti	48·17
Tungsten	W	184·4
Uranium	U	240·0
Vanadium	V	51·4
Ytterbium	Yb	173·0
Yttrium	Yt	89·0
Zinc	Zn	65·40
Zirconium	Zr	90·5

THE CLASSIFICATION OF THE ELEMENTS.



Anomalous:
Cobalt = 59·00
Nickel = 58·70
Tellurium = 127·5

Unclassified:
Helium = 2·0 or 4·0?
Argon = 19·94 or 39·9?
Praseodymium = 140·5
Neodymium = 143·6
Samarium = 150·0
Gadolinium = 156·0
Terbium = 160·0
Erbium = 166·0
Thulium = 170·0
Ytterbium = 173·0

chloride yields 40·101 per cent of platinum and 30·671 per cent of potassic chloride,—the means of the closely agreeing results of Seubert and Halderstadt,—while, according to Halberstadt, potassic platinbromide yields 25·915 per cent of platinum, and 31·591 per cent of potassic bromide. Disregarding the weight of the complex salt, and assuming that $\mathrm{KCl}=74{\cdot}595$, and $\mathrm{KBr}=119{\cdot}095$, it is easy to calculate the respective values 195·06 and 195·39 for platinum. The mean of these two values, 195·2, is given below, instead of Clarke's 194·89. The possible occlusion of potassic halide by the complex salt may render even 195·2 too low; but more investigation is evidently needed to prove this.

The same errors may enter into the work on other platinum metals; indeed Seubert (*Ann. Chem.*, *Liebig*, cclxi., 262) admits that traces of water were contained in some of his salts, but he applies no correction for this serious cause of inaccuracy. Since, however, Clarke's method of combining the discordant results seems more nearly to eliminate the error in these cases, his values for these elements are but little changed in the table.

Feeling wholly unable to decide the present controversy between the two conflicting values (184·9 and 184·0) now proposed for tungsten, I have chosen the mean 184·4 as a compromise which cannot be much more than 0·3 per cent out of the way (compare Hardin, *J. Am. Chem. Soc.*, xix., 657, 1897.

Uranium, the highest of all the atomic weights, is one of the least satisfactorily determined. Recent investigation upon this subject at Harvard seems to show that all the published data are complicated by constant errors, which, however, sometimes partly eliminate one another: accordingly the round number 240, instead of Clarke's 239·59, is printed in the table. The discussion is better deferred until our work has taken more definite shape.

Besides these seven elements, there are seventeen more whose atomic weights, as given in the following table, differ from the results of Professor Clarke's computations by one part in a thousand or more. As none of the seventeen values is known certainly to within one part in five hundred, and some of them are probably at least as much as 1 per cent in error, differences in these cases will excite no especial remark. The elements are:—Cerium, columbium, erbium, gadolinium, gallium, glucinum, indium, lanthanum, neodymium,* osmium, palladium, praseodymium, samarium, scandium, thorium, ytterbium, and zirconium. This is by no means a complete list of the uncertain elements, but only of those for which the data admit of slightly different interpretations.

It is rather unfortunate that most classified tables of the elements omit the fractional parts of the atomic weights, for these fractions will undoubtedly play an essential part in the ultimate solution of the de-Chancourtois-Newlands-Mendeleeff-Meyer mystery. In order to present a modern table which will supply these omissions, as well as afford at a glance an approximate idea of the probable error in each case, I have repeated the values in the natural order. From the classified table have been omitted several elements whose atomic weights and properties are uncertain; their presence in the system serves rather to obscure well-known relations than to elucidate new ones. That this procedure is an omission of incompleteness is evident; the last part of the table is at best a lame affair. The form proposed by Thomsen (*Ztschr. Anorg. Chem.*, ix., 190) is perhaps the most generally satisfactory of the current modes of arrangements, but his last row is unwieldy both for printing and for thinking. In the accompanying table a compromise has been adopted which cannot fail to be comprehensible; it is not my purpose here to enter into the arguments regarding the adequacy of the various forms.

This table will be reprinted, with any changes which may be necessary, every year. Since the commencement of the work I have been glad to hear of the appointment of a Committee by the German Chemical Society to accomplish a similar purpose, the American Chemical Society having for several years possessed such a Committee. The matter cannot receive too much intelligen-examination.

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* Since the publication of this paper in the *Proceedings of the American Academy*, H. C. Jones has published a research upon the "dymia" which far exceeds in accuracy and completeness the vague statements of their first separator. Oddly enough, the new values are the old ones interchanged. While it is impossible to say how nearly the new figures represent the peculiarly elusive values in question, they carry with them much greater weight than the old ones, and are given, as far as the first decimal place, in the accompanying table. (See *Am. Chem. Journ.*, xx., p. 345). The value 142 for the mixture "didymium" is also given for convenience in the calculation of analyses in which it is not possible to separate the twins.

NOTICES OF BOOKS.

Radiation. An Elementary Treatise on Electromagnetic Radiation, and on Röntgen and Cathode Rays. By H. H. FRANCIS HYNDMAN, B.Sc. (Lond.). With a Preface by Professor SILVANUS P. THOMPSON, D.Sc., F.R.S.

THE introductory note by Professor Thompson is sufficient to stamp the book as beyond the usual sphere of recent publications on this subject, and its perusal fully justifies the expectation.

Although professedly elementary, the subject-matter is very sound, and the manner in which it is handled carries with it a refreshing sense of originality that makes the book very easy reading.

Starting with the fundamental principles of Radiation, Part I. is devoted to Material Vibrations, longitudinal and transverse; and in Part II. the ether theory is very clearly and simply elucidated, occupying about 120 pages of valuable and interesting matter. The latter half of the book is devoted to Cathode and Röntgen radiation, and is thoroughly up-to-date, and what strikes one very forcibly is the complete absence of sensationalism which usually characterises publications on this subject; there is not even a radiograph of a hand or the picture of an induction coil by a popular maker!

The references to the original papers make this section very valuable. There is a short chapter on Becquerel's Rays, and finally an account of the experiments of Gustave le Bon on "Dark Light."

While we consider the book to be one of the best that has appeared of its class since Röntgen's discovery, there are, unfortunately, one or two errors, chiefly clerical, that we must point out. An amusing one is on page 46, where the ether is said to be "incomprehensible": this, although possibly correct, is probably a misprint for incompressible. On page 167 we read "Radiant electrode matter, or negative rays of Crookes." The term "Radiant electrode matter" is not due to Crookes, whose contention is that the Radiant matter of a highly exhausted vacuum tube is not necessarily electrode matter, but may be purely gaseous. At page 200 we think the author is rather hasty in the statement that Cathode rays "do not affect the eye, and produce no sensation on the skin"; and on page 208 there is a serious mistake, which looks as if a proof-sheet had got astray, for, commencing to describe the "focus tube" as designed by Mr. Herbert Jackson, the description goes on to another and totally different piece of apparatus, where the Cathode stream is focussed on to the glass wall of the tube. This is unfortunate, and will cause some little confusion to the uninitiated. On page 210 a reference is given to *Nature*, June, 1896, which should have been July—describing a form of X ray tube which is said to be of a "markedly improved form," but we cannot help thinking that those who know the difficulties of producing sufficiently high vacua for Röntgen rays would hesitate to accept the recommendation.

These, however, are small matters, and beyond the error on p. 208, already referred to, in no way detract from the value of the book. While commending it to any who wish for sound elementary instruction on the principles of Radiography, we can heartily indorse the concluding sentence of Professor Thompson's preface—"It is much too good to be of use to one whose highest aim is to pass examinations."

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvi., No. 25, June 20, 1898.

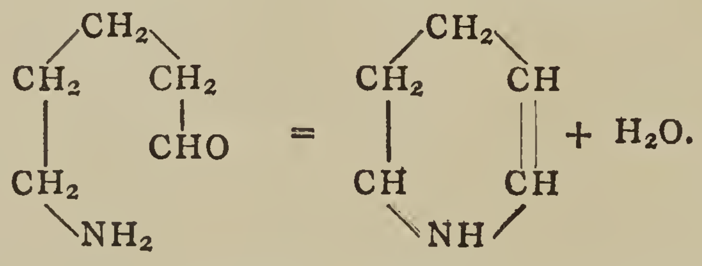
Boiling-point of Liquid Ozone.—L. Troost.—Already inserted in full.

The Preparation of Crystallised Calcium.—Henri Moissan.—Already inserted in full.

A New Gas in the Atmosphere.—W. Ramsay and M. W. Travers.—This has already been noticed in our columns.

Sulphoantimoniates of the Alkaline-earthy Metals.—M. Pouget.—In following up the study of the sulphoantimoniates, the author has acted on the alkaline-earthy sulphides with sulphide of antimony, and has found that a number of compounds are formed with the salts of barium, strontium, and calcium. All these compounds are easily oxidised in contact with air, and should therefore be prepared in a current of hydrogen. The reaction permits of the preparation of ortho- and pyro-sulphantimoniates. Analogies between calcium and strontium are found in the pyro-compounds, and between strontium and barium in the ortho-compounds.

Pyridic Bases.—Marcel Delépine.—Most methods of synthesising the pyridic derivatives consist in the elimination of water between an amine function and an aldehydic or acetonic function, and thus allowing them to become joined to the nitrated functions derived from the aldehyds. The author has here restricted himself to the study of pyridine itself and to that of its hydrides. These first terms give very little direct synthetical action which could be considered as resulting from the unique junction between the aldehydic and the nitrogenised function; but one extremely important one exists, inasmuch as it constitutes at the same time the bond which unites the fatty and the pyridic series; it is the synthesis of tetrahydropyridine, or piperideine, by δ-aminovaleraldehyd,—



It is true that piperidine, C_5H_9N, is only well known under its polymerised form, $(C_5H_9N)_2$; but the author thought it advisable to open the research with a view to finding the thermochemical reactions which exist in this series. For this purpose he took up the study of pyridine, piperidine, chloropiperidine, piperideine, and δ-aminovaleraldehyd, with the results given in this paper.

Some Bases derived from Piperidine.—G. André.—The author has made a fresh study of the bases derived from piperidine and the ethylenic carbides, such as ethylene, propylene, and its isomer, trimethylene. He has also examined the new oxygenised derivatives of glycerin. All these bodies are bi-nitrated; those derived from the carbides do not contain any oxygen, but those derived from glycerin do. The bases examined were:—Dipiperidine-ethylene, $(C_5H_{10}N)_2C_2H_4$; dipiperidine-methylethylene, $C_5H_{10}N.CH(CH_3).CH_2.C_5H_{10}N$; dipiperidine-trimethylene, $C_5H_{10}N.CH_2.CH_2.CH_2.C_5H_{10}N$; and several others.

Bromised Derivatives of Morphine.—H. Causse.—The bromised substitution of morphine as a definite compound seems to be limited to the fourth degree. This result agrees with certain experiments on oxidation which will be published later on. When bromising takes place in concentrated hydrobromic acid, the action of the bromine is regular, and gives rise to crystalline compounds; finally, the tetrabromomorphine behaves as a base or an acid. This last property is not possessed by tribromomorphine.

Some New Aromatic Diurethanes from Piperazine.—MM. Cazeneuve and Moreau.—In a recent paper the authors described their work on the phenylic, gaïacolic, naphtholic α- and β-derivatives, they now complete this series by the description of the derivatives of orthochloric phenol, thymol, and the ortho-, meta-, and para-cresols.

Action of Chlorine on Chloride of Ethylene in the presence of Chloride of Aluminium. The Chloridation of Acetylene.—A. Mouneyrat.—A long paper, not suitable for abstraction; but the author describes his experiments carried out with a view to determining the constitution of the product resulting from the chlorisation of $(CH_2Cl—CH_2Cl)$ in the presence of this synthetic agent.

Synthesis of Symmetric Tetramethylglutaric Acid.—E.-E. Blaise.

Crystallised Compound of Acetylene with Cuprous Chloride.—M. Chavastelon.—When, in the preparation of pure acetylene, we pour hydrochloric acid on moist acetylide of copper, we notice that the latter dissolves without any appreciable disengagement of gas if we take care to cool the mixture during the operation, but under the influence of heat acetylene is produced. It must therefore be admitted that there is a temporary formation of a compound—destroyed by heat—of acetylene and chloride of copper. It can be formed in a hydrochloric solution of cuprous chloride or in an aqueous or alcoholic solution of cupric chloride in the presence of copper.

THE CHEMICAL NEWS.

Vol. LXXVIII., No. 2030.

ETHERION: A NEW GAS.*

By CHARLES F. BRUSH.

On the 3rd inst. Mr. Brush read a paper on his newly-discovered gas before the Chemical Society of Cleveland, U.S.

The author commenced by saying that, at the very start, he encountered difficulties in the absence of a means to produce the very low pressures he needed, and to surmount these difficulties he invented the best mechanism for this purpose yet used.

When he came to examine air at very low pressures and under certain conditions for its heat conductivity, in his chart plotting he was brought to draw several lines, the dotted ones in the chart given herewith, which could be accounted for by no lines of the known gases, like the continuous lines of the diagram. Thus the existence of a new gas was indicated.

Since *Etherion*, as Mr. Brush named the new gas, has no known chemical effect on familiar elements, and will thus not burn or form combinations, it would probably always have remained unknown did it need to depend for discovery on the usual chemical experiments. It was by his entrance into a new field of investigation that Mr. Brush encountered evidence of its existence.

The chart herewith reproduced is that which accompanied his full paper, read first before the American Association for the Advancement of Science, at Boston, on August 23, 1898. An extract from this paper follows:—

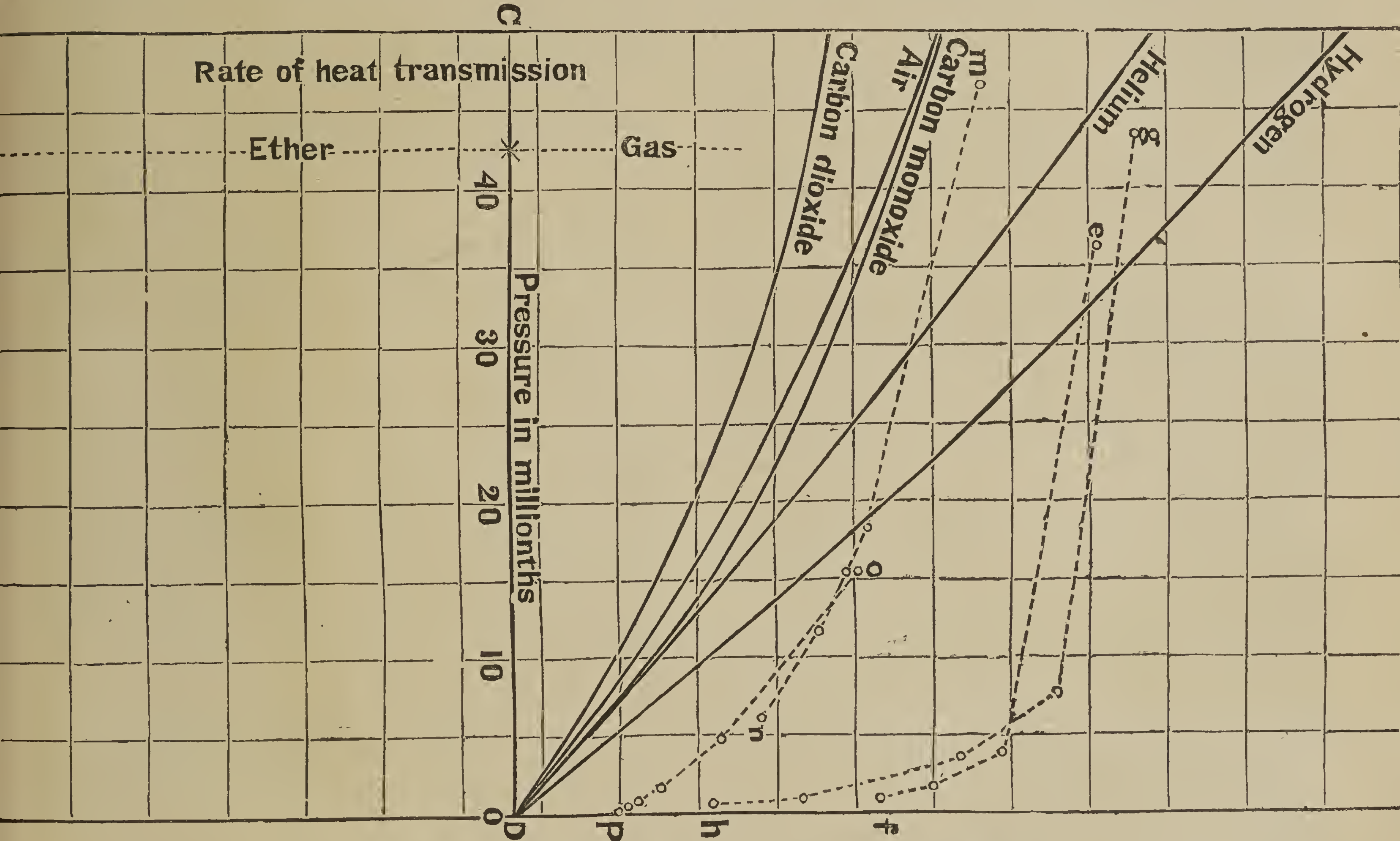


Chart showing Relative Heat Conductivity of Gases.

"The purpose of this purely preliminary is to announce the discovery of a new gas, presumably elementary, and possessed of some extraordinary properties. It is a constituent of the atmosphere, and is occluded by many substances. Its chief characteristic thus far ascertained is enormous heat conductivity at low pressures. In order to appreciate this phenomenon it is necessary to consider the heat conductivity of some of the well known gases.

"A year ago I had the honour to read before this Section a paper on the transmission of heat by gases, and illustrated by numerous curve sheets showing the heat conductivity of several gases at all pressures from atmospheric down to the best vacuum obtainable; also an allied paper on the measurement of small gaseous pressures.

"The apparatus used for the described experiments in heat transmission consisted in part of a long-stemmed thermometer hanging in a long-necked glass bulb, the bulb of the thermometer being in the centre of the glass bulb. Two bulbs were used for different experiments, the larger one 112 m.m. in diameter, the smaller one only 20 m.m. A tank of water and crushed ice under the bulb was adapted to be raised when desired, so as to immerse the bulb in the cold mixture. The neck of the bulb was connected with an air pump capable of reducing the internal pressure to a very small fraction of a millionth of atmospheric pressure; also with an elaborate pressure gauge adapted to measure small pressures with very great precision, and a barometric gauge for measuring larger pressures.

"The present chart shows curves representing the heat conductivity of several gases, from fifty-millionths of atmospheric pressure downward.

"A very brief account of the circumstances which led to the discovery of the new gas may not be out of place. I had long been engaged in high vacua experiments, and had observed that glass apparatus, when highly exhausted and heated, involved gas for an indefinite length of time,

—rapidly at first, then slower, but never stopped until the temperature was reduced. On cooling, rapid re-absorption always took place, but was never complete; indicating that two or more gases had been evolved by heating, one of which was not absorbed on cooling. In other words, the absorption was selective.

"The truth of this conclusion was abundantly demonstrated subsequently. However, the percentage of re-absorbed gas was so large that I used a small quantity of pulverised glass, in several experiments, to absorb a part of the residual gas after the highest attainable exhaustion was reached. The pulverised glass was always lead glass like that of the apparatus, and was heated nearly red-hot for several hours before and during the final exhaustion.

"During these experiments a curious phenomenon was noted; the pulverised glass lost its snowy whiteness. This I thought must be due to reduction of some of its lead; probably by hydrogen evolved on heating. If so, I argued that the hydrogen must have been absorbed from the atmosphere since the manufacture of the glass; and its presence in the glass, if proved, would be a long step toward proving the normal presence of hydrogen in the atmosphere.

"Following the line of experiment thus suggested, I prepared a quantity of pulverised soda glass free from lead, and placed about 120 grms. of it in a large combustion tube connected with the apparatus already described. The combustion tube was adapted to be heated by a gas furnace with automatically regulated gas supply, so as to be maintained at any desired temperature.

"While prepared to make analysis in the usual way of the gas evolved by the pulverised glass in case it appeared in sufficient quantity, I relied chiefly on its heat conductivity for the detection of any large proportion of hydrogen in the last few millionths, not being prepared at that time for spectroscopic examination; and thinking that perhaps some hydrogen might be evolved in the last stages of exhaustion before heating, I tested the conductivity of the residual air from time to time as the preliminary exhaustion progressed.

"When the exhaustion approached a good vacuum, an astounding phenomenon developed. At 36-millionths pressure, the residual gas conducted heat twice as well as air, and nearly as well as hydrogen, at 3·8 millionths it conducted seven times as rapidly as hydrogen, at 1·6 millionths fourteen times, and at 0·96 of one millionth twenty times as rapidly. These results are plotted in the curve *e f*. I did not carry the exhaustion lower than 0·96 m. At this pressure, the time of cooling of the thermometer from 15° to 10° was only 177 seconds, while pure hydrogen would have required 288 seconds.

"Evidently a new gas of enormous heat conducting capacity was present, mixed with the last small portion of air. It must have come from the pulverised glass, and probably formed only a small fraction of the mixture. The last cubic centimetre of gas pumped out was collected, and upon subsequent analysis of it nothing but air was found.

"The discovery of the new gas as above outlined was made nearly a year and a half ago, on March 10th, 1897. On the following day the pressure had increased to nearly five-millionths; while the time of cooling of the thermometer, instead of diminishing as usual with increase of pressure, had risen from 177 seconds to 245 seconds, showing that the new gas had largely disappeared. This was subsequently found to be due to absorption by the phosphorous pentoxide used in desiccation.

"Long-continued moderate heating of the pulverised glass caused the evolution of some air, much carbon dioxide and hydrogen, some carbon monoxide, and more of the new gas. The selective absorption which occurred on cooling was confined almost wholly to the hydrogen and the new gas. After further moderate heating and thorough exhaustion, I raised the temperature, continued the exhaustion, and got the results embodied in the curve *g h*, showing that much of the new gas was present: the conductivity at 0·38 of a millionth, the last station in the curve, being twenty-seven times that of hydrogen! Several days of high heating, with frequent exhaustion, failed to wholly deprive the pulverised glass of its new gas, though the output was greatly diminished. For this and other reasons I believe that the new gas resides in, and not simply on, the surface of glass.

"A rejuvenation of pulverised glass by exposure to the air, in connection with the results obtained by the diffusion of air, leaves no room for doubt that the new gas is a constituent of the atmosphere.

"Several other substances than glass were examined, and nearly all found to contain the new gas.

"When the new gas was present the form of the conductivity curves was very different from those of the known gases, the effect of the new gas becoming more prominent as the pressure was reduced. I do not doubt that this was due to the interference of the heavier and slower moving molecules of the ordinary gases always mixed with the new gas. When the new gas is obtained in a state of purity, I expect to find its curve of heat conductivity similar to those of hydrogen and helium, but with immensely increased ordinates.

"Believing that the new gas is very much lighter than air or hydrogen, and may therefore be separated from the atmosphere by successive diffusions, I have spent several months in experiments with this end in view. Quite recently my efforts have been crowned with most promising success. The difficulty has been to find a suitably porous septum; one free from holes, and sufficiently fine grained to prevent more than a very slow passage of air, while a considerable surface is exposed to the atmosphere on one side, and to a fairly good vacuum on the other.

"The best results have been obtained with porous porcelain having its superficial pores nearly closed by suitable treatment. A tube of this kind, closed at one end, was connected with the apparatus, and the whole kept exhausted to a pressure of 1·3 m.m. About 19 c.c. of gas was diffused per hour. After thirty-six hours, the diffusion tube was shut off, the exhaustion continued, and data for the *m n* curve obtained. It was found impracticable to carry the exhaustion below 6 millionths, because of the presence of moisture, which interfered with the action of the pump—no desiccating agent being used. As both phosphorus pentoxide and soda-lime absorb the new gas, they cannot be used for desiccation.

"If the exhaustion had been carried as far as in the curve *o p*, it is probable that a higher conductivity than in that curve would have been shown, *i.e.*, a conductivity more than forty-two times that of hydrogen, or something like a hundred times that of air. Here we have the heat conductivity of air at very low pressure increased something like a hundredfold by one diffusion.

"I have not yet tried a secondary diffusion, but feel confident that successive diffusions of air will afford a practicable means of obtaining the new gas in a state of approximate purity."

HELIUM IN THE ATMOSPHERE.

The following letter appeared in last week's *Nature*:—

"The letter of Mr. Baly in your issue of last week, corroborating the statement of Friedlander and Kayser that helium is a constituent of the atmosphere, induces me to put on record a further confirmation of the accuracy of this observation. Having had the opportunity, on June 20 last, of examining samples of the more volatile portions from liquid air, which had been handed to me by Prof. Dewar, I had no difficulty in seeing the lines of helium in them. Further, a sample of the helium separated by Prof. Dewar from Bath gas (following the discovery of Lord Rayleigh) undoubtedly contained the substance called neon.

"In giving these facts I am only confirming the observations of Prof. Dewar given to me in letters accompanying the samples of gas.

William Crookes."

October 11.

FURTHER EXPERIMENTS ON THE ABSORPTION OF THE RÖNTGEN RAYS BY CHEMICAL COMPOUNDS.*

By Dr. J. H. GLADSTONE, F.R.S., and WALTER HIBBERT.

This paper has for its object a description of experiments on the absorption of Röntgen rays by metals and metallic salts. It is in continuation of what has been reported at the two previous meetings of the British Association.

During the past year we have had two purposes in view. 1. To perfect the quantitative methods employed for estimating the comparative intensity of radiographs taken simultaneously. 2. To determine whether the amount of absorption is fairly an atomic phenomenon, or whether the amount of rays absorbed by a compound body depends to any extent on its physical condition or manner of combination.

We have again employed the Lummer-Brodhun photometer, and have endeavoured to insure as much regularity in the amount of exposure as possible, by placing the objects that were simultaneously exposed at a considerable distance from the radiating point, usually about 15 inches, and by rotating them during the experiment. We believe that in this way the effect upon the sensitive plates can be determined within ± 2 per cent. In order further to reduce the effect of unavoidable irregularities, each experiment was usually repeated about six times, and the mean was taken. By the kindness of Mr. Wimshurst one of his machines was sometimes employed, as it was found to give a steadier effect than the Ruhmhorff coil.

Among the results arrived at were the following:—

Reflection and Refraction.—A polished plate of glass was compared with the same glass in a finely powdered condition, care being taken that there was the same quantity of material on a unit of area. The radiograph of the powdered glass was about 3 per cent deeper than that of the polished plate. Hence reflection or refraction would appear not to have been entirely absent.

Solid or Liquid.—To determine whether the passage from a liquid to a solid condition affects the amount of absorption, experiments were made with paraffin in the two states. The result was practically the same in each case.

Combination or Mixture.—Pounded crystals of the double sulphate of copper and ammonium gave practically the same absorption as a mere mixture of the two constituent salts in a similar state of division. Hence the chemical union had no influence on the result.

Metal and Oxide.—Finely divided metallic copper was found to absorb about 2 per cent more rays than either the black oxide, CuO, or the red oxide, Cu_2O, when the depth of the mass penetrated contained the same amount of metal. It would appear from this as though the oxygen, instead of adding a little to the general result, as might have been expected, had the opposite effect. A similar result had been previously obtained when the comparison was made with sheet copper.

Change of Atomicity.—The above experiments showed also that the change of atomicity in these two oxides of copper did not produce any notable difference. The same result was also obtained when the two oxides of mercury, the red HgO, and the black Hg_2O, were similarly examined. A third instance of a like character was obtained with lead. The yellow litharge, PbO, and the puce coloured peroxide, PbO_2, were identical in their absorptions. Another experiment, to determine whether change of atomicity caused any difference, was made with ferrous and ferric oxalates, FeC_2O_4 and $Fe_2(C_2O_4)_3$. In order to form a comparison between the two, so much oxalic acid was added to the ferrous salt as was necessary to equalise the amount of carbon and oxygen in the two bodies. Again the result was almost identical.

Carbon and Hydrocarbons.—The former experiment on the absorption of carbon and various hydrocarbons was repeated with additional precautions, and varied as to length of exposure, distance from the radiating point, &c. The hydrocarbons were chosen so as to represent both crystalline and liquid substances, varying also in saturation from amyl hydride, which is a saturated compound, through turpentine, benzene, and naphthalene, to anthracene, the furthest removed from saturation. The depth of the substance penetrated always contained the same amount of carbon. In almost every instance the uncombined carbon was found to absorb a little more than the equivalent quantity of any of the hydrocarbons. The following table gives the final average results of a large number of comparisons, carbon always being taken at 100.

Carbon	Solid, black	C	100
Anthracene ..	,, white	$C_{14}H_{10}$	96
Naphthalene ..	,, ,,	$C_{10}H_8$	93
Amyl hydride ..	Liquid, colourless	C_5H_{12}	96·5
Turpentine ..	,, ,,	$C_{10}H_{16}$	95
Benzene	,, ,,	C_6H_6	94·5

Though the amount of hydrogen, and the consequent degree of saturation, is extremely various, there does not appear to be a correspondence in the variations of the power of absorbing the X rays; but the variations scarcely exceed the limit of error of experiment.

The experiments of this year therefore confirm the opinion previously expressed, that the absorption of the Röntgen rays by a compound body is almost wholly dependent upon the absorption exercised by its constituents. It is little, if at all, modified by their physical condition, or by change of atomicity, or by other differences of combination.

The question, however, forces itself on our minds, whether these small differences of results may not be due to the presence in the Röntgen radiations of small quantities of rays, which, though they have passed through aluminium foil, have properties somewhat analogous to ordinary light. It is evident that if a small amount of sunlight were to become mixed with the Röntgen rays it would increase the apparent absorption by the pounded glass, or by opaque metals, or black carbon. We venture to think that if such supposed rays could be entirely sifted away, the Röntgen radiations in their passage through a body would be affected merely by the nature of the atoms forming it, and that the law that the absorption by a compound is the mean of the absorption due to its several constituents would be not only proximately but absolutely true. The answer to this question must depend upon further research.

In some of the later experiments we have used a simple apparatus for testing the grade of the Röntgen rays employed. In a sheet of thick lead a rectangular window was cut, and over one-half of the window we fastened a piece of thin platinum or tin foil. An aluminium "stepped" scale was adjusted over the other half of the window, and the whole inserted between the radiating tube and an ordinary fluoroscope. On looking into the fluoroscope the rectangular window was seen as a patch of light, each half differently illuminated. But by sliding the aluminium scale to and fro, a position was found for it at which the two halves of the window became uniformly illuminated. The particular "step" of aluminium which was then in position was the index of the "grade" of the rays.

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* Abstract of a Paper read before the British Association (Section B), Bristol Meeting, 1898.

Since this paper was read we find that Professor Röntgen has recently described a somewhat similar apparatus, the chief difference being that he brings many of the aluminium "steps" in view at the same time.

SOME RESEARCHES ON THE THERMAL PROPERTIES OF GASES AND LIQUIDS.*

By SYDNEY YOUNG, D.Sc., F.R.S.

GASES under moderate or low pressures are characterised by the simplicity of the laws relating to the variation of their volume with temperature and pressure. But when the pressure is greatly increased, these laws no longer hold good; at constant temperature the product pv, instead of remaining constant, diminishes until a minimum is reached, and at still higher pressures increases again, and this increase continues up to the highest pressures that have been reached.

A most important advance in the explanation of the behaviour of compressed gases and of liquids was made just twenty-five years ago by Van der Waals, who, taking into account the two facts (1) that the molecules of a gas attract one another, (2) that they occupy a finite volume, and are not mere mathematical points, proposed the formula—

$$\left(p + \frac{a}{v^2}\right)(v - b) = \mathrm{RT}$$

in place of the simple one $pv = \mathrm{RT}$. The formula of Van der Waals expresses very well the general relations of pressure, temperature, and volume for both gases and liquids, but does not give the actual values with sufficient accuracy, and many attempts have been made to alter it in such a way as to bring about a better agreement. It is noticeable that at constant volume the formula becomes $p = \mathrm{KT} - c$, where K and c are constants, depending on the volume, and this simple relation has been found to hold good for gases by Amagat, and for both gases and liquids by Ramsay and myself. Within the last few years I have investigated the behaviour of a hydrocarbon, isopentane (*Proc. Phys. Soc.*, xiii., p. 602), through a very wide range of volume (1·6–4000 c.c. per grm.), and of normal pentane through a smaller range, and the data so obtained have led Rose-Innes (*Proc. Phys. Soc.*, xv., p. 126; xvi., p. 11) to a formula—

$$p = \frac{\mathrm{RT}}{v}\left\{1 + \frac{e}{v + k - gv^{-2}}\right\} - \frac{l}{v(v + k)},$$

based on the simple one $p = \mathrm{KT} - c$, which reproduces the observed isothermals from the largest volume to about 3·4 c.c. per grm., with a maximum error of slightly over 1 per cent.

A complete investigation of this kind requires, however, a large amount of time, and can only be carried out with very stable substances of comparatively low critical temperatures, and it occurred to me about eleven years ago, that a careful study of certain generalisations, deduced by Van der Waals from his formula, might yield valuable results, and perhaps indicate the direction in which the formula requires alteration.

The generalisations may be stated thus:—If any two substances, A and B, are compared at pressures, $\mathrm{P_A}$ and $\mathrm{P_B}$, proportional to their critical pressures, $\pi_{0\mathrm{A}}$ and $\pi_{0\mathrm{B}}$, their boiling-points (absolute temperatures), $\mathrm{T_A}$ and $\mathrm{T_B}$, will be proportional to their critical temperatures, $\theta_{0\mathrm{A}}$ and $\theta_{0\mathrm{B}}$, and their volumes, both as liquid, $\mathrm{V_A}$ and $\mathrm{V_B}$, and as saturated vapour v_A and v_B, will be proportional to their critical volumes, $\phi_{0\mathrm{A}}$ and $\phi_{0\mathrm{B}}$. It would follow from this that at "corresponding" pressures the ratios of the actual to the theoretical density of saturated vapour, $\frac{\mathrm{D}}{\mathrm{D}_1}$, should be the same for all substances.

It is convenient to speak of the ratio of the pressure to the critical pressure as the "reduced" pressure, π, the actual pressures, $\mathrm{P_A}$, $\mathrm{P_B}$, being called "corresponding" pressures.

I proposed, therefore, to determine the vapour pressures and the specific volumes (both as liquid and as saturated vapour) of a considerable number of substances from low temperatures to their critical points, and in the first place I chose some compounds of elements belonging to the same group in the periodic table, as it seemed possible that some points of interest might thus arise. The first substances I examined were the four monohaloid derivatives of benzene, as well as benzene itself (*Trans. Chem. Soc.*, lv., p. 486), and the result of the investigation was to show that, when the haloid derivatives are compared together, the generalisation, as regards temperature and pressure, hold good accurately; but there is this peculiarity about these compounds, that their critical pressures are equal, or very nearly so, and therefore "corresponding" pressures are in this case equal pressures. The critical pressure of benzene itself is different, and when the hydrocarbon is compared with any of its haloid derivatives, the differences between the temperature ratios are much greater. As regards the volume ratios, the differences are small in all cases.

The only other substances, bearing on the periodic arrangement of the elements, which have been yet examined are the tetrachlorides of carbon and tin (*Trans. Chem. Soc.*, lix., p. 911). The critical pressures differ considerably, and the relationship resembles that of the normal paraffins to each other, which will be referred to later. Many of the chlorides of the elements are very hygroscopic, and attack mercury at high temperatures, and it was thought better to postpone their further examination, and to obtain the data for a few series of homologous organic compounds. Up to the present, in addition to the three lowest alcohols, investigated by Ramsay and myself, ten esters (*Trans. Chem. Soc.*, lxiii., p. 1191) and four paraffins (*Ibid.*, lxvii., p. 1071; lxxi., p. 446; lxxiii., p. 675; *Proc. Phys. Soc.*, xiii., p. 602) have been studied, and with the exception of the alcohols, it has been observed in every case (and the same remark applies to the tetrachlorides of carbon and tin) that the ratios $\frac{\mathrm{T}}{\theta_0}$ at any reduced pressure increase with rise of molecular weight. No definite relation is observable between the molecular weights and the ratios $\frac{\mathrm{V}}{\phi_0}$ and $\frac{v}{\phi_0}$ in the case of the esters, but with the three normal paraffins (pentane, hexane, and heptane) and the two tetrachlorides, the ratios $\frac{v}{\phi_0}$ increase and $\frac{\mathrm{V}}{\phi_0}$ diminish slightly with rise of molecular weight. With the alcohols, on the other hand, the ratios $\frac{\mathrm{T}}{\theta_0}$ and $\frac{\mathrm{V}}{\phi_0}$ are irregular and $\frac{v}{\phi_0}$ diminish.

Another point of interest is the comparison of isomeric compounds, but up to the present, the only two pairs of isomers investigated are methyl butyrate and isobutyrate, and normal and iso-pentane. In both cases there is a clear relationship between the ratios and the constitution, the normal and iso-compounds standing to each other in much the same relative positions as a higher and lower normal paraffin.

It is worthy of remark that the volumes of a grm. of all four paraffins are nearly the same (4·266–4·303) at the critical point.

Looking at the data for the twenty-six substances examined, it is evident that they may be divided into groups:—1. Benzene and its haloid derivatives, ether

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* A Paper read before the British Association (Section B), Bristol Meeting, 1898.

the tetrachlorides, and the paraffins. 2. The ten esters. 3. The alcohols. 4. Acetic acid. The members of Group 1 may be regarded as normal; the deviations of the ratios from constancy are small, though, as pointed out, they exhibit certain regularities; in Group 2 the values of $\frac{v}{\phi_0}$ are rather higher, and of $\frac{V}{\phi_0}$ rather lower than in Group 1; in Group 3 the ratios $\frac{T}{\theta_0}$ and $\frac{v}{\phi_0}$ are very high; for acetic acid $\frac{T}{\theta_0}$ and $\frac{V}{\phi_0}$ are high, but $\frac{v}{\phi_0}$ very low. The marked differences between the alcohols and acetic acid, and the large deviations in both cases, are probably to be accounted for by the fact that the molecules of the alcohols at moderate temperatures are polymerised in the liquid—but not the gaseous—state, whilst with acetic acid there is polymerisation in both states.

The ratios $\frac{D}{D'}$ at the critical point should, according to Van der Waals, be the same for all substances, the molecules of which undergo no dissociation or polymerisation, and he gives the value of this ratio as $\frac{8}{3}$ or $2{\cdot}\dot{6}$. Now the ratio depends on the constant b in the equation—

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT,$$

and Van der Waals takes b to be four times the actual volume of the molecules in unit mass of substance; O. E. Meyer, however, contends that $b = 4 \times \sqrt{2}$ times the volume of the molecules, and it has been pointed out by Heilborn and by Guye that, if that is so, the ratio $2{\cdot}\dot{6}$ should also be multiplied by $\sqrt{2}$, which would give the value 3·77. It is remarkable that the mean value for the twelve substances in Group 1 is 3·77, from which it may be concluded that the molecules of these substances in the critical state are simple like those of the gas. At the same time it is to be noticed that with the three normal paraffins and the two tetrachlorides $\frac{D}{D'}$ shows a slight increase with rise of molecular weight.

The ratios for the ten esters are a little higher (3·87 to 3·95); decidedly higher for the alcohols, especially methyl-alcohol (4·52 – 4·02), and much higher for acetic acid (5·00). It would appear from this that the molecules of the alcohols and acetic acid are polymerised to a considerable extent at the critical point, and this conclusion is supported by the generally abnormal behaviour of these substances, and agrees with that of Ramsay and Shields, that in the liquid state at moderate temperatures their molecules are decidedly complex, whilst those of the majority of the compounds examined by them are probably simple.

I hope to continue the investigation of the paraffins and other hydrocarbons in order to obtain further light on the points referred to. and it will be of interest to compare the molecular volumes at the critical points, and at a series of reduced pressures.

The accurate determination of the critical constants is a matter of great importance. It is best to employ an apparatus similar in principle to that of Andrews, in which the temperature, pressure, and volume can be altered at will; though the critical temperature may be determined with but small error in a sealed tube, if the quantity of liquid taken is such that its critical volume is approximately equal to the capacity of the tube. With a pure substance, free from air, two independent determinations of the critical temperature should certainly not differ by 0·1°, unless the temperature is above 300°, when the experimental difficulties are greater. The error in the determination of the critical pressure should not exceed 0·2 per cent, but the critical pressure is greatly affected by the presence of even very small quantities of impurity (and, of course, of air), and in comparing two specimens of the same substance, one of which is known to be pure, the agreement of the critical pressure is probably the most delicate test of the purity of the other.

The only method yet known by which the critical volumes can be accurately determined is the indirect one based on the "law of diameters" of Cailletet and Mathias. These physicists made the very important discovery that the mean densities of liquid and saturated vapour for any "normal" substance are a linear function of the temperature (or $D = D_0 - a\,t$ where D = the mean density), and since, at the critical point, the two densities are equal—or rather there is only one—the value of D at that point gives the critical density, from which the critical volume is, of course, easily calculated. I have been able to show that the law of Cailletet and Mathias holds good with great accuracy right up to the critical point (with normal pentane observations were taken to within 0·05° of the critical temperature), for all the compounds examined except the alcohols. It has, in view of these results, been suggested, I think justly, by M. Guye, that a serious deviation from the law may be taken as a proof of the existence of molecular dissociation or polymerisation.

It is true that a few years ago I was under the impression that a direct determination of the critical volume was possible, and the values obtained do, indeed, bear as nearly constant ratio to the true critical volume, but they are about 14 per cent too low. The probable explanation of the error has been given by M. Gouy, who pointed out that, at the critical point, a substance is so extremely compressible, that in a long column the density increases very considerably from top to bottom, owing to the pressure exerted by the substance itself.

In the course of these researches ample proof has been obtained that the views of Andrews regarding the behaviour of a substance in the neighbourhood of the critical point are correct, and also that the vapour pressure of a pure substance is quite independent of the relative volumes of liquid and vapour. These points are referred to because they have been called in question by several observers during the last few years.

Two of the substances examined attack mercury at high temperatures, and it was therefore impossible to determine either their vapour pressures or specific volumes by the methods employed for the other liquids. The difficulty, as regards vapour pressure, was overcome by sealing a wider tube to the lower end of the volume tube, and using such a quantity of liquid that during the observations the lower end of the column was always in the wider and cold part of the tube. The height of the column of mercury in the tube must, under these conditions, be calculated (*Trans. Chem. Soc.*, lix., 917).

A method of determining the specific volumes of both liquid and saturated vapour in a sealed tube was also devised (*Ibid.*, lix., 37). When the specific volumes of the liquid are already known, this method, in a simplified form, is very convenient for determining the specific volumes of saturated vapour (*Ibid.*, lix., 125; *Proc. Phys. Soc.*, xiii., 617).

It is obviously necessary that, in order to obtain trustworthy results, pure substances must be employed, and, indeed, more time has been spent in the preparation of the pure substances than in the determination of their physical constants. The difficulties met with in the fractional distillation of liquids, more especially in the separation of pure hydrocarbons from petroleum, have led to an extended study of this subject, and both new apparatus (Chem. News, lxxi., 177; *Trans. Chem. Soc.*, lxxi., 440) and new methods of procedure (*Phil. Mag.*, 1894, p. 8) have been devised; it has thus been possible to separate perfectly pure normal and iso-pentane (B. P. 27·95° and 36·3°) from the complex mixture of hydrocarbons in American petroleum.

ACTION OF WATER AND SALINE SOLUTIONS ON METALLIC IRON.

By ROBERT MELDRUM, F.C.S.

Action of Water.

The following experiments were made with the view of ascertaining whether the oxidation of pure iron takes place in chemically and biologically pure water; also if the general rule that iron is unacted upon by alkaline solutions holds good. The trials were made in 4-oz. stoppered bottles, free from lead. The distilled water was freshly prepared, and during the time under observation the trials were freely exposed to the light. Six feet of polished piano-wire, weighing 4·11 grms., was used in each experiment; it being made into a coil and fully immersed.

1. Town water, of 16° hardness, with about 25 c.c. air in bottle. In a few days the metal was coated with a yellow deposit, there being at the bottom a large yellow precipitate, the under layer of which was bluish black or very dark green.

2. Distilled water with about 25 c.c. of air. At the end of four weeks the wire became partly corroded; large precipitate at bottom, the lower part of which was bluish black, especially where it touched the metal, the upper portion being yellow.

3. Distilled water with bubble of air in bottle. In three weeks heavy yellow precipitate at bottom.

4. Distilled water with bubble of air. In four weeks the wire was dull; yellow precipitate at bottom, with shining transparent scales.

5. Distilled water, free from NH_3 and therefore CO_2, with air bubble. In a few weeks the iron was very dull; dirty yellow precipitate at bottom, intermixed with innumerable transparent scales.

6. Distilled water with about 15 c.c. of air. Wire coated with black tarnish; large brown precipitate at bottom, containing numerous shining scales. The glass was highly iridescent where it touched the metal.

7. Distilled water with no air bubble. Water became cloudy in ten minutes, yellow in one hour, and at the end of five hours there was an orange precipitate at the bottom.

8. Distilled water free from NH_3, and therefore CO_2, with air bubble in bottle. Iron corroded; yellow precipitate in three hours; little change in twenty-four hours.

9. Distilled water boiled in 4-oz. flask plugged with cotton wool, cooled, and charged with sterilised iron wire; half air and half water in flask. Water became yellow in twenty-four hours; large precipitate in several days; iron partly rusted.

10. Distilled water boiled for an hour in 8-oz. flask plugged with wool while boiling: when cold, put in bright sterilised wire. About 50 c.c. air in bottle. Wire rusted very slightly; no yellow deposit in four days.

11. Distilled water boiled for one hour in 8-oz. flask. Placed in wire and plugged with cotton wool during boiling. Wire rusted badly in twenty four hours; in several days, much yellow precipitate.

12. Distilled water boiled in 8-oz. flask. While still warm, placed wire in same; filled with boiling water to neck and corked, thus leaving no air bubble in flask. After four weeks the liquid was only slightly yellow, but no deposit on wire.

13. Distilled into stoppered bottle of 130 c.c. capacity until completely full NH_3, and therefore CO_2, free water. Placed therein six feet of wire; after placing, there remained in the bottle a very small air bubble. In four hours a yellow precipitate formed, and at the end of twenty days the air bubble had increased in size to about 1 c.c., the wire having become coated with black tarnish. The yellow precipitate had increased in volume, and contained both ferrous and ferric iron, and after ignition weighed 0·0115 grm., and when shaken innumerable small glistening iridescent scales appeared; the inside of the bottle was covered with iridescent lustre.

14. Same experiment as above, but with 12 feet of wire. Same results. This contained an excessive quantity of lustrous plates, some being of very large area. Weight of ignited deposit, 0·01 grm.

From the above experiments it will be seen that the oxidation of iron takes place in the absence of bacteria and other forms of life, NH_3, and CO_2. In the best of the experiments free O and N must have been present in the water, but to a very small extent; and, as yet, it is therefore an open question as to whether it is the water or dissolved oxygen which acts on the metal.

When a coil of tarnished or bright wire is placed in pure distilled, soft, hard, or any other kind of water, and exposed to light, the following is what usually takes place:—There is immediately formed a white cloud around the metal, which gradually increases until, in about fifteen minutes, the whole liquid becomes cloudy and then yellow, and in about three or four hours a yellow precipitate falls to the bottom. Wire, after immersion for several weeks, always appears to be slightly brittle, and possesses a smell of ozone. When the surface of iron exposed is great in proportion to the volume of water, and especially on free contact with the air, the bottles become internally coated with a film which communicates a highly iridescent lustre to the glass. The small glistening plates found among the hydrated oxides appear under the microscope to be detached parts of this transparent matter. Whether these films are due to bacteria, decomposition of the glass, or deposition of iron compounds I am unable to say.

Action of Saline Solutions.

In the following series of experiments the wire was immersed in the solution, the bottles being half-full of liquor. The substances were pure, and were all alkaline to phenolphthalein with the exception of sodium and potassium hydrogen phosphates.

Calcium Hydrate.— Saturated clear solution; wire quite bright at end of four weeks; no deposit.

One per cent Sodium Peroxide.—Wire quite bright at end of ten days; no deposit.

One per cent Sodium Hydrate.—Wire quite bright at end of four weeks; no action.

One per cent Potassium Hydrate.—Wire quite bright at end of four weeks.

One per cent Barium Hydrate.—No action in ten days.

One per cent Ammonium Hydrate.—Iron tarnished yellow in four weeks.

One per cent Sodium Carbonate.—Iron tarnished yellow in four weeks.

Five per cent Strontium Hydrate.—No action in four weeks.

One per cent Sodium Acid Carbonate. — Immediate action; dirty yellow precipitate in twelve hours. Iron turned black.

One per cent Sodium Biborate.—No action on metal in four weeks, but slight white sediment at bottom.

One per cent Sodium Hydrogen Phosphate.—A precipitate begins to form in fifteen minutes; large precipitate in twenty four hours.

One per cent Potassium Hydrogen Phosphate. — Same remarks as above.

One per cent Sodium Metaphosphate.—Wire covered with air bells in fifteen minutes, and slightly dull in four days. In ten days the upper portion of the solution is yellow, the lower portion green.

One per cent Sodium Pyrophosphate.—Immediate action; orange sediment in twelve hours; wire coated with deposit in six days.

One per cent Potassium Carbonate.—In six days large rust growth on metal, with a few particles at bottom.

One per cent Potassium Biborate.—Small white precipitate in ten days.

One per cent Potassium Borate.—In ten days a large rust growth on wire, but no precipitate.

It is clear from these experiments that all alkaline salts do not prevent the oxidation of iron. It is remarkable that sodium peroxide should have no action, whereas potassium carbonate produced much. From this it appears that alkaline potassium salts act on iron to a much greater extent than those of sodium. The bicarbonates were decomposed very rapidly, with the formation of *large* white precipitates, eventually turning yellow.

ON THE
ANALYSIS OF MOLYBDENUM COMPOUNDS.

By HARRY BREARLEY.

I. *The Estimation of Molybdenum.*

Chatard's Process. — Chatard proposed to estimate molybdenum by adding lead acetate to the solution of an alkaline molybdate. The precipitated molybdate of lead, after washing and drying, is to be ignited—the paper separately—at a temperature not beyond a low red heat.

Chatard (Chemical News, xxiv., 175) illustrated the process by test analyses on a solution of pure soda molybdate, but does not mention whether the solution was acid or neutral. Fresenius ("Quant. Anal.," i., 289) mentions the process, but says that it is only applicable for solutions of *pure* alkaline molybdate.

Being in need of a reliable and simple process of estimating molybdenum as separated from diverse metallurgical compounds, Chatard's, amongst others, was tried. As the early results were so promising, the general bearings of the method were worked out, and are here set down.

Starting with a solution of pure soda molybdate, it was found that from neutral solutions precipitation with neutral lead acetate was accurate, but that from very faintly alkaline solutions part of the excess of the precipitant is decomposed, though hardly noticeably so if—as Chatard points out — only a slight excess of acetate is used. In any case it is troublesome to have to perform operations in accurately neutralised solutions; the first step, therefore, was to determine whether the precipitation might not be made from a slightly acid solution.

In determining the influence of the following compounds, an amount of alkaline molybdate equivalent to 0·1 grm. molybdenum was used in every case. The figures given represent the amount of Mo recovered, and by their greater or less approximation they indicate the influence of the added compound.

Influence of Acetic Acid.—The lead molybdate, which from neutral solutions is rather granular, becomes more and more powdery as the acidity increases and tends the more to pass through the filter. This fact would probably impose a limit on the excess of acid which could be used. The volume of solution precipitated from was was always about 250 c.c.

2	5	10 c.c., 33 per cent acetic acid.
0·1000	0·0999	0·0998 Mo recovered.

All further precipitations were made from solutions containing about 2 c.c. of free acetic acid.

Excess of Lead Acetate.—If neutral solutions are adhered to the danger of large excesses of lead acetate, in case a faint alkalinity has been overlooked, is evident. In acid solutions no such precautions need be taken.

40	100 percentage excess $Pb\bar{A}_2$
0·1001	0·1000 Mo recovered.

The prolonged washing of the more powdery precipitates with pure hot water tends, in the later stages, to give opalescent washings. This difficulty is entirely overcome by washing with a solution of 1 c.c. $Pb\bar{A}_2$* in 500 c.c. of water just acidulated with acetic acid.

Igniting the Paper Separately.—By inference from the behaviour of lead sulphates it may have been concluded that the ignition of the $PbMoO_4$ apart from the paper was necessary.

As the separation always involves time, trouble, and with powdery precipitates some danger of loss, it was thought worth while to observe the error which comes of igniting the precipitate and paper together. Whether the paper and precipitate was previously dried in the water-bath, or folded wet and placed in a crucible at the mouth of a muffle, or separated according to Chatard's instructions, it made no matter; the results were always the same. But this much must be said :—If the more expeditious method of drying in front of the muffle be adopted, then the early ignition should be allowed to take place at the lowest temperature practicable, otherwise patches of the paper are imperfectly decarbonised, and the higher temperatures needed to complete the ignition are disallowed by the instability of the lead molybdate.

In order to determine whether lead molybdate could be reduced by carbonaceous matter, half a grm. of finely powdered wood charcoal was placed in the solution either before or after precipitating the $PbMoO_4$. The moist precipitate is thus intimately mixed with carbonaceous matter, and takes a considerable time to ignite. Three separate tests, after igniting to constant weight and correcting for the charcoal ash, gave 0·0993 gr. of molybdenum instead of 0·1000 gr.

Temperature of Ignition.—It should not be inferred that ignition at temperatures beyond the minimum employable are attended with disastrous results. For general technical purposes a long range of temperature is admissible.

This latter statement is founded on numerous experiments, all showing that prolonged ignition at high temperatures causes only a very slow decrease in the weight of $PbMoO_4$. The following is a typical case :—Ignited at a low red heat the weight of $PbMoO_4$ was 0·3685 gr. By gradually increasing the temperature it fell to 0·3675. By pushing the muffle to full redness—at which temperature soda carbonate in an adjacent crucible readily fused—the weight after ten minutes fell to 0·3665. After remaining at this temperature (850—900° C.) for six hours, the weight was only reduced to 0·3650—a loss altogether of just under 1 per cent.

Influence of Alkaline Salts.—The salts were formed in the soda molybdate solution by adding a measured quantity of strong acid, neutralising with soda carbonate or ammonium hydrate as the required salt demanded.

	5 c.c.	10 c.c. acid used.
Soda chloride	0·1000	0·0998
,, nitrate	0·1001	0·1004
Ammon. nitrate	0·1003	0·1001
,, chloride	0·0998	0·0999

With the non-volatile salts great care was taken to eliminate possible compensatory errors. Unlike many precipitates, particularly gelatinous and flocky ones, the lead molybdate does not appear to hold associated alkaline salts very tenaciously. Thus we found that prolonged washings gave the same results as only three or four washings, and, to further confirm this observation, we have frequently re-dissolved the ignited $PbMoO_4$ in dilute hydrochloric acid, neutralised with ammonia, added an excess of acetic acid, a few more drops of lead acetate, and repeated the whole operation. This second precipitation never sensibly altered the result. In observing the influence of a series of metallic compound I have had regular occasion to make use of this repeated precipitation, chiefly for confirmatory purposes, but occasionally on account of the purifying nature of the process. We shall refer to it subsequently merely as re-precipitating the lead molybdate.

Ammonium acetate, of such strength as is obtained by neutralising 0·880 ammonia with 33 per cent acetic acid,

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* Strength of $Pb\bar{A}_2$ solution = 7·896 grs. crystals per litre.

will be seen later to be an important reagent. Its influence in large quantities was therefore noted.

10 c.c.	30 c.c. ammon. acetate.
0·1000	0·1002 Mo recovered.

Like acetic acid it causes the precipitate to be powdery. With the larger amounts the filtrate needs re-passing through the pore-clogged paper.

It must be admitted that, in comparison with other processes, the behaviour of Chatard's under other than ideal circumstances is very satisfactory, and that, the above results being accepted, it should no longer be regarded as a process available only for the estimation of molybdenum in pure alkaline molybdates.

At this point we were satisfied that Chatard's process would meet our requirements, but—partly from curiosity, and partly, if possible, to avoid the separating of associated metals in some molybdenum alloys which occasionally engage us—we decided to observe the interference which the presence of some of the commoner metals would introduce. This kind of work is somewhat monotonous. We are of opinion, however, and we are supported in this alike by observation and experience, that one knows a method well only when he knows its limitations. Those limitations once determined, the knowledge serves the double purpose of minimising the danger of error and of eliminating a number of separations which, not uncommonly, introduce greater errors than they obviate.

The Interference of some Metals.

Attempts have been made to precipitate lead molybdate in the separate presence of about twenty metals. For the sake of brevity these may be treated of in classes.

First are those which exert no practical interference, and occasion no trouble beyond more careful washing or a re-precipitation of ignited $PbMoO_4$. These, and the results obtained with them are set forth in—

TABLE I.

Interfering metal.	Grm. added.	
	0·10	0·20
Manganese	0·1003	0·1003
Copper	0·0999	0·1001
Cobalt	0·1004	0·1001
Nickel	0·1003	0·1004
Zinc	0·1004	0·0999
Magnesium	0·1002	0·1009
Mercury (ic)	0·0999	0·1000
Uranium	0·1017	0·1015

The figures given are those obtained from the first precipitation of the lead molybdate. In every case the $PbMoO_4$ was re-precipitated, whether there was cause to suspect impurity or not.

Manganese and Copper.—The colour of pure lead molybdate (ignited) is creamy. Any compound then whose oxide is dark coloured is at once indicated. From the presence of manganese the ignited precipitate is darkened; but on treating with nitric acid and lead peroxide, so as to convert the Mn_3O_4 into permanganate, only a very faint colouration was observable. A similar remark applies to copper.

Cobalt.—Precipitates formed in cobalt solutions are greyish when ignited. On re-dissolving in strong HCl the traces of Co form a green solution. The colour disappears on diluting. I have found this reaction with cobalt and strong HCl to indicate as small an amount as 0·00005 grm. cobalt. After being purified by re-precipitation the $PbMoO_4$ rarely contains more than that negligible amounts.

This colour test could probably be used to indicate the extent to which a precipitate was contaminated with cobalt, in the same way as traces of iron are estimated by the sulphocyanide colouration. My experience has shown that only such amounts of cobalt are associated with the first precipitation of the lead molybdate as would pass unnoticed if it were not for the strong grey colour which the cobalt imparts to the precipitate.

It is impossible to wash *all* the cobalt from the first precipitate. Smith and Bradbury (*Berichte*, xxiv., 2930) have pointed out that cobalt forms a small quantity of a bluish-white precipitate in concentrated solutions of sodium molybdate; the fact that the moist precipitate has a *very faint* purple cast indicates that such a compound may be responsible for the greyness of the ignited $PbMoO_4$. The further fact that the greyest of the precipitates never weighed appreciably more than it should supports this view.

Nickel and Zinc.—On neutralising the acid solution of zinc and molybdenum a precipitate is formed. The usual excess of acetic acid mainly dissolves this precipitate, but a faint cloudiness—probably a molybate of zinc—remains. We find it to be perfectly safe to disregard this appearance so long as it is not more than an opalescence, if the lead acetate be added in excess to the cold solution. If the cloudiness is considerable the neutralisation is stopped short, and the remaining free HCl decomposed with ammonium acetate. Nickel exhibits this cloudiness in a lesser degree.

Mercury and Uranium.—A precipitate forms before neutralisation is effected. In the case of mercury it is dissolved slowly on heating with the excess of acetic acid; but in the case of uranium it is only slowly, if at all, effected by such treatment. In either case the warm solution immediately clears on adding ammonium acetate.

Uranium is the only element in Table I. which contaminates the precipated lead molybdate to any serious extent. The ignited precipitates are always yellowish-brown, and on treating with hydrochloric acid the colouring is at once dissolved. By re-precipitating the error may be reduced to half per cent, but the $PbMoO_4$ needs repeatedly precipitating to separate the last traces of uranium.

Volumetric Processes.

Molybdenum may be estimated indirectly by adding an excess of lead acetate, filtering off the lead molybdate, and applying to the filtrate any of the trustworthy methods of determining lead.

The determination of the lead by means of potassium chromate and ferrous sulphate (*Journ. Am. Chem. Soc.*, Nov., 1895) has given good results, but it needs careful working. All things considered this is not so rapid as the previously described gravimetric one, and is certainly much less delicate.

Schindler (CHEMICAL NEWS, lviii., 61) has described a volumetric process for the estimation of molybdenum in which lead acetate is added to an acidified solution of a molybdate until the latter ceases to give any colouration when mixed on a white-cupped tile with tannin.

We have experimented with this method on solutions of pure alkaline molybdates, and can readily aver that it gives rapid and approximate results. As the end of the reaction is approached the indications are rather uncertain.

It has been said that, in neutral or faintly acid (acetic) solutions, the precipitated lead molybdate is granular and easily filterable. In using Schindler's method we support or correct its conclusions in the following manner:—

Add lead acetate and use the tannin reaction as long as it is available. The degree of accuracy thus obtainable will vary little more than 1 per cent from the truth. Pour a little of the hot solution through a ribbed paper, and test the filtrate first with lead acetate, and if necessary with soda molybdate. Generally the first test will show that some molybdenum is still unprecipitated, and the intensity of the cloudiness, after a little experience, indicates approximately how much. The one or the other reagent is added as required, and the solution tested in this way until with absolute certainty it can be said that neither soda molybdate nor lead acetate is present in other than negligible quantities. As the solution is passed and repassed through the same filter until the end is reached, there is no loss through the absorption of the paper. And, finally, it is always open, if desired, to complete the gravimetric operation.

This process is shorter than the gravimetric one, and on pure solutions it is equally accurate. We have not observed the interference of large amounts of metallic salts.

The test proposed as a supplement to Schindler's is a very delicate one. In a faintly but decidedly acid (acetic) solution, measuring 400 c.c., a distinct cloudiness is formed by lead acetate when only 0·0001 grm. of Mo is present,—that is, one part in four million parts of solution, a degree of accuracy not to be surpassed by the most fastidious working of the gravimetric process.

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending September 30th, 1898.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To Major-General A. De Courcy Scott, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, October 10th, 1898.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Sept. 1st to Sept. 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined by us during the month all were found to be clear, bright, and well filtered.

The serious deficiency in the rainfall still continues. Rain fell at Oxford on six days only during September, the total fall being only 0·38 inch. The thirty years' average is 2·43 inches; we thus have a deficiency of 2·05 inches, bringing the total deficiency for the year up to 8·22 inches.

Our bacteriological examinations of 258 samples have given the results recorded in the following table; we have also examined 39 other samples, from special wells, stand-pipes, &c., making a total of 297 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	485
New River, filtered (mean of 26 samples) ..	12
Thames, unfiltered (mean of 26 samples) ..	2957
Thames water, from the clear water wells of five Thames-derived supplies (mean of 128 samples)	32
Ditto ditto .. .. highest	612
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 26 samples) ..	3378
River Lea, from the East London Company's clear water well (mean of 26 samples) . ..	27

Our bacteriological examinations of the 297 samples have been quite satisfactory. The extraordinary deficiency in the rainfall in the Thames Valley, which now amounts to 44·5 per cent from the 1st of January, as our tables show, has had no effect in causing deterioration in the water supply of the Metropolis.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

THE

ACTION OF LIGHT UPON DYED COLOURS.[*]

(Continued from p. 193).

Black Colouring Matters.

Class I.—Very Fugitive Colours. (Wool).

Azo Colours.

Wool Book XIV.

Acid Colours.—

4. Violet Black. From p-phenylene-diamine, with α-naphthylamine and α-naphthol-sulphonic acid NW. S. and J. III. 502.

Direct Cotton Colours.—

1. Nyanza Black B. From p-phenylene-diamine-azo-α-naphthylamine and amido-naphthol-sulphonic acid γ.
2. Tabora Black R. Constitution not published.

Notes.—During the first "fading period" Violet Black changes to a dull vinous red colour.

Class II.—Fugitive Colours. (Wool).

Azo Colours.

Wool Book XIV.

Acid Colours.—

6. Azo Nigrine R. From phenol-disulphonic-acid-azo-α-naphthylamine and β-naphthol.
12. Wool Black. From amido-azo-benzene-disulphonic acid and p-tolyl-β-naphthylamine. S. and J. III. 139.
13. Jet Black G. Constitution not published.
19. Phenylene Black. From α-naphthylamine-disulphonic-acid-azo-α naphthylamine and diphenyl-m-phenylene-diamine. S. and J. III. 152.
21. Anthracite Black R. From α-naphthylamine-disulphonic acid and α-naphthylamine-azo-diphenyl-m-phenylne diamine.
26. Azo Acid Black B. Constitution not published.
27. Azo Acid Black G. Constitution not published.

Direct Cotton Colours.—

10. Direct Deep Black T. Constitution not published.
11. Columbia Black 2B. Constitution not published.
12. Columbia Black B. Constitution not published.
13. Oxy Diamine Black N. Constitution not published.
14. Union Black S. Constitution not published.
16. Oxy Diamine Black SOOO. Constitution not published.
18. Columbia Black R. Constitution not published.

Direct Cotton Colours Developed.—

1. Diamine Black BH. From benzidine and γ-amido-naphthol-sulphonic acid and amido-naphthol-disulphonic acid H. Developed with Fast Blue Developer AD.
2. Diazo Black B. From benzidine and α-naphthylamine-sulphonic acid L. Developed with β-naphthol.

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[*] Report of Committee, consisting of Dr. T. E. Thorpe (Chairman), Professor J. J. Hummel (Secretary), Dr. W. H. Perkin, Professor W. J. Russell, Captain Abney, Professor W. Stroud, and Professor R. Meldola. (Drawn up by the Secretary). Read before the British Association (Section B), Bristol Meeting, 1898.

*3. Diamine Black ROO. From benzidine and β-amido-naphthol-sulphonic acid. Developed with Fast Blue Developer AD. S. and J. III. 187.

4. Diazo Black R. Constitution not published. Developed with β-naphthol.

5. Diazo Black H. Constitution not published. Developed with β-naphthol.

*8. Diamine Black BO. From ethoxy-benzidine and amido-naphthol-sulphonic acid γ. Developed with Fast Blue Developer AD. S. and J. III. 229.

Oxazine Colours.

Basic Colours.—

1. Cotton Black. Constitution not published.

Natural Colouring Matters.

Mordant Colours.—

Limawood (Fe). Cæsalpinia echinata (wood).

Notes.—The following colours acquire a reddish or purplish tint during the fading process:—Azo Acid Blacks B and G, Columbia Blacks B and R, Union Black S, Oxy-diamine Black SOOO, Diamine Black RO and BO. An olive tint is acquired by Direct Deep Black T.

(To be continued).

TRANSFORMATION OF CHEMICAL ENERGY INTO ELECTRIC ENERGY.[*]

By Prof. F. FOERSTER.

(Concluded from p. 192).

The original construction of the Borchers cell presented a series of defects which became more and more marked after prolonged use. We cannot here go into the details of the research which Borchers undertook in the endeavour to eliminate these defects, however useful they may have been to future workers on the subject. The greatest difficulty was to succeed in getting as perfect a contact as possible between the gas, the electrolyte, and the electrode, without allowing the solutions charged with the two gases to become mixed. The best results were obtained by stopping the continued current of air and by using an oxidising material which would be periodically regenerated by the atmospheric air. As an oxidising material Borchers took Weldon mud (manganite of lime mixed with a solution of chloride of lime). This mud is placed in an iron or lead box, which at the same time serves as an electrode; a flattened cell of refractory clay kept away from the air is plunged into the mud. This cell contains a horizontal plate of carbon which also serves as an electrode, and an acid solution of chloride of copper, through which a current of carbonic oxide is passed. The battery lasts until all the binoxide of manganese is reduced to the state of oxide. This can then be easily regenerated by blowing in more air. If we take precautions to maintain the solution of the chloride of copper, acid, and that of the manganite alkaline, the working of the cell will be very regular, and its electromotive force 0·6 volt with an external resistance of about 50 ohms. Borchers himself is far from wishing to attribute any commercial value to his cell, such as it is described. The question as to how far the oxidation of the carbonic oxide can be pushed in such a cell has not yet been decided. But it may be permissible to regard Borcher's process as a method for the preparation of oxalic acid, starting from carbonic oxide, a method which at the same time produces electric energy, and which therefore may some day lead to the solution of the problem. The researches of Borchers took place in the laboratory of Prof. Nernst at Gottingen, and in that of the Elberfelder Farbenfabriken.

A comparison of Borcher's experiments with those of Reed (*Zeit. f. Elect.*, iii., p. 87) will show us what different lines have been followed in the endeavour to construct a commercial galvanic battery. Reed based his research on the following fact. Sulphurous acid reacts on sulphuretted hydrogen, giving rise to the formation of water and sulphur. This reaction is followed by a disengagement of electric energy when carried out in a suitable apparatus constructed on the principle of a gas cell.

As for the two gases they are obtained in the following manner. Sulphur is burnt in a retort to produce sulphurous acid, which is passed into the cell; the heat given off by this combustion is sufficient to vapourise the sulphur and make the carbons which are in the retort red-hot. The vapour of the sulphur gives sulphide of carbon, which is mixed while hot with steam, giving rise to the following decomposition:—$CS_2+2H_2O=2H_2S+CO_2$. The sulphuretted hydrogen and the carbonic acid pass into the other compartment of the cell, where the electric current is generated by the reaction—$2H_2S+SO_2=3S+2H_2O$. We thus see that the three atoms of sulphur which were necessary to produce one molecule of sulphuretted hydrogen and one molecule of sulphurous acid are regenerated, and that the final result of all these operations is the transformation of the carbon into carbonic acid by the intermediary of sulphide of carbon. As the transformation of carbon into carbonic acid gives off 97,000 calories, and as the reaction between the sulphuretted hydrogen and the sulphurous acid gives off 25,000 calories, we see that 61 per cent of the heat of combustion is disposable for being transformed into electric energy.

From the above data Reed estimates the electromotive force of his cell at 0·63 volt. His apparatus, however, only gave him 0·36 volt. This disagreement may be partly explained by the fact that calculations of electric energy based on thermochemical data are never very exact. According to Reed the importance of his process consists less in its practical value than in its principle. He believes that the true method of obtaining the electric energy of carbon will be to employ an intermediary material which, like sulphur, would serve to make the oxidation of the carbon indirect. But in the presence of the results he obtained this assertion would appear to be a little pretentious.

We can see that the problem of making a carbon battery is still far from being solved. But it is possible that the solution of the more general problem of the commercial transformation of chemical into electric energy may be elucidated by the aid of other chemical reactions besides the combustion of the carbon. Several interesting researches have already been made in this direction.

We know that a cell with carbon electrodes, one of which is placed in a solution of chloride of protoxide of copper and the other in chloride of cupric oxide, gives an electric current when we pass chlorine gas through the cupric chloride; the current lasts as long as any unoxidised chloride of the protoxide remains. If this can be continually reproduced by means of a reducing gas we should get a practically continuous galvanic cell.

Andrews found (*Zeit. f. Elect.*, iii., p. 88) that sulphurous acid (but not carbonic oxide) can be used for this purpose. The sulphurous acid is transformed into sulphuric acid, and it is evident that it is the oxidation of the sulphurous acid which causes the electric energy of the cell.

No doubt it is now impossible to commercially isolate the sulphuric acid which is formed in this process; but we can do away with the copper salts if instead we use carbon tubes plunged into dilute sulphuric acid, and if by means of these tubes we introduce chlorine and sulphurous acid under high pressure.

The following reaction here serves for the production of electric energy—

$$SO_2+2H_2O+Cl_2 = H_2SO_4+2HCl,$$

and we obtain an electromotive force of 0·5 volt when the circuit is closed through a resistance of 1 ohm. It now remains to find a means of replacing the chlorine by the

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[*] *Moniteur Scientifique*, Series 4, vol. xii., July, 1898.

oxygen in the air, so as to produce simultaneously pure sulphuric acid as well as electric energy.

As far as we can judge at the present day the formation of hydrochloric acid from its elements would still be the easiest reaction to employ for the production of electric energy by chemical means. The more the electrolytic manufacture of the alkalis progresses the more important becomes the question of the utilisation of the chlorine set at liberty in these electric processes.

While in the old Leblanc process the chlorine was considered as a valuable secondary product which could be produced in large quantities, it becomes in the electrolytic processes an encumbrance if we cannot find new applications for it. In the earlier times there was generally produced one ton of chloride of lime for each two or three tons of caustic soda, while the chlorine given off in the manufacture of the same quantity of soda by the electrolytic process gives nearly five tons of chloride. It is probable that a corresponding increase in the consumption of chloride of lime for bleaching purposes, disinfection, &c., is very unlikely. On the other hand, the electrolysis of the alkaline chlorides gives at the cathodes equivalent quantities of hydrogen, the utilisation of which is yet an interesting problem. The idea of combining the chlorine and the hydrogen naturally presents itself for the purpose of obtaining hydrochloric acid, of which the Leblanc process is at present the principal source.

The preparation of hydrochloric acid from chlorine and hydrogen has already been the subject of many patents, all of which point to the direct union of the two gases one with the other; but it is evident that we thus lose chemical energy which might be transformed into electricity if we could but construct a suitable apparatus in which the two gases could be combined indirectly. The energy that could be collected in this manner is fairly considerable, since the galvanic combination, Cl, ClH, H, gives with a great external resistance an electromotive force of 1·37 volts. If we could only succeed in making a commercial battery of this type the future of electrolytic processes for the manufacture of soda would be assured, even in face of the Solvay process. Thus by retransforming a part of the gas given off as hydrochloric acid we should obtain the electric current as a secondary product. The remainder of the chlorine would be converted into chloride of lime, while the corresponding quantity of hydrogen could, if advisable, be compressed.

These considerations naturally give many points for elucidation, but they show that the problem of the transformation of chemical into electrical energy can be attacked from more than one side.

THE IODOMETRIC DETERMINATION OF MOLYBDENUM.*

By F. A. GOOCH and JOHN T. NORTON, Jun.

A PROCESS for the iodometric determination of molybdic acid, which consists in treating a soluble molybdate in a Bunsen distillation-apparatus with potassium iodide and hydrochloric acid, has been advocated by Friedheim and Euler (*Ber. d. D. Chem. Gesell.*, xxviii., 2066). According to this process the molybdate, containing from 0·2 grm. to 0·3 grm. of molybdenum trioxide, is treated with from 0·5 grm. to 0·75 grm. of potassium iodide, and enough hydrochloric acid, of sp. gr. 1·12, to fill two-thirds of the flask of the apparatus. The liquid is warmed until heavy vapours of iodine fill the flask, and then boiled until iodine vapour is no longer visible and the colour of the liquid residue is a clear green. The iodine liberated is collected in the distillate and titrated with sodium thiosulphate, every atom of iodine found indicating presumably the reduction of a molecule of molybdic acid to the condition of the pentoxide Mo_2O_5,

It was pointed out in a former article from this laboratory (Gooch and Fairbanks, *Amer. Journ. Sci.*, IV., ii., 156), that greater precaution than was taken by Friedheim and Euler is necessary in order that the reduction may proceed according to theory, and that the iodine collected may serve as a reliable measure of the molybdic acid. It was found that the green colour of the liquid comes gradually, and that it may develop distinctly before the molybdic acid is fully reduced. It was found, also, that since even a trace of oxygen liberates iodine from the hot mixture of potassium iodide and hydrochloric acid of the strength employed, it is not sufficient to rely upon the volatilisation of iodine to expel the air originally in the apparatus, but that it is essential to conduct the distillation in an atmosphere devoid of oxygen. The suggestion was made, therefore, that the operation should be carried on in a current of carbon dioxide, and that the mixture, constituted definitely, should be boiled between stated limits of concentration which were determined by experiment. It was found that when amounts of a soluble molybdate containing less than 0·3 grm. of molybdenum trioxide are treated with potassium iodide, not exceeding the theoretical proportion by more than 0·5 grm., and 40 c.m.^{3} of a mixture of the strongest hydrochloric acid and water in equal parts, the reduction proceeds with a fair degree of regularity, and is practically complete when the volume has diminished to 25 c.m.^{3} If the operation is properly conducted in an atmosphere of carbon dioxide, it was shown that the iodine in the distillate may be trusted to indicate the molybdic acid within reasonable limits of accuracy. It appeared, however, that too great an excess of potassium iodide tends to induce excessive reduction, and that the same tendency shows when the liquid is concentrated to too low a limit.

To this criticism Friedheim took exception (*Ber. d. D. Chem. Gesell.*, xxix., 2981), and contrasted, to their disadvantage, our results by the modified method with those of Friedheim and Euler by the original method. It became necessary, therefore, to point out (Gooch, *Amer. Journ. Sci.*, IV., iii., 237) the fact that of the results published by Friedheim and Euler, upon which reliance was placed to prove the liability of their method, five out of seven in one series and one out of five in another series had been calculated incorrectly from data given. Another series of six determinations was, however, apparently faultless in this respect. More recently (*Zeit. f. Anorg. Chem.*, xv., 454) Euler has explained that the errors were not really arithmetical. Two of them may be presumed, inferentially, to be due to careless copying or proof-reading; and four, we are told by Euler, were introduced into the series by mistake, and actually represent (as Prof. Friedheim kindly informs him) the analysis of a sample of ammonium molybdate of undetermined constitution,—that is to say, the figures now given by Euler represent the original percentages of molybdenum trioxide which had been changed by some unconscious process from—

80·62 per cent to 81·85 per cent.
80·71 ,, 81·69 ,,
80·63 ,, 81·66 ,,
80·78 ,, 81·78 ,,

Curiously enough Euler's corrected figures, as given here, are still affected by trifling arithmetical errors of from one to four units in the second decimal place. The agreement of these results among themselves is no proof of the correctness of the process of analysis. The great variation between the average percentage of molybdenum trioxide in ammonium molybdate as found by Euler in a molybdate of known constitution, and the percentage of the trioxide as found by Friedheim (if we understand Euler aright), may be due conceivably to either or both of two causes, viz., the change of material analysed and the change of operator or conduct of the operation. We shall show in

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* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, vol. vi., 1898.

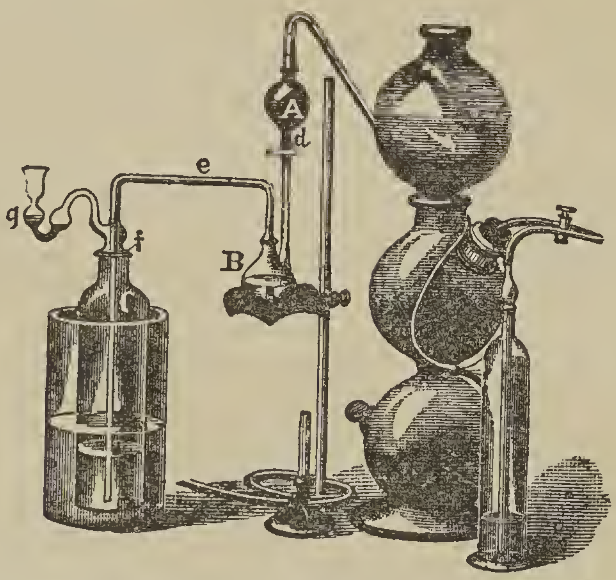
the following account of our work that the exact control of the conditions of treatment, along the lines laid down formerly, is actually essential to the reduction of molybdic acid according to the theory of the process.

Our experiments were made with ammonium molybdate twice re-crystallised from the presumably pure salt. The constitution of the preparation was determined by careful ignition *per se*, and, for greater security, with sodium tungstate free from carbonate. It contained 81·83 per cent of molybdenum trioxide.

The potassium iodide which we used was prepared by acting with re-sublimed iodine upon iron wire, and precipitating by potassium carbonate—the proportions of iodine and iron having been adjusted to secure the formation of the hydrous magnetic oxide of iron. The filtrate from the iron hydroxide gave on evaporation and crytallisation potassium iodide which was free from iodate.

The hydrochloric acid was taken of sp. gr. 1·12, because this is the strength used by Friedheim and Euler.

The sodium thiosulphate employed was taken in nearly decinormal solution, and was standardised by running it into an approximately decinormal solution of iodine which had been determined by comparison with decinormal arsenious acid made from carefully re-sublimed arsenious oxide. We chose this method of standardising—the introduction of the thiosulphate into the iodine—rather than the reverse operation, in order that the conditions of the actual analysis might be followed in the standardisation.



The distillation apparatus was constructed with sealed or ground joints of glass wherever contact with iodine was a possibility. It was made by sealing together a separating funnel A, a 100 c.m.^{3} Voit flask B, a Drexel wash-bottle C, and a bulbed trap *g*, as shown in the figure. Upon the side of the distillation-flask B was pasted a graduated scale by means of which the volume of the liquid within the flask might be known at any time. Carbon dioxide, generated in a Kipp apparatus by the action of dilute hydrochloric acid (carrying in solution cuprous chloride to take up free oxygen) upon marble previously boiled in water, was passed through the apparatus before and during the operation, so that it was possible to interrupt the process of boiling at any point of concentration, to remove the receiver by easy manipulation, to replace the receiver, and to continue the distillation without danger of admitting air to the distillation flask.

In experiments to be described—(1) to (5) of the table—the proportions of potassium iodide and molybdic acid, and the strength of the hydrochloric acid recommended by Friedheim and Euler were retained. The essential change of condition is the removal of atmospheric air from the distillation flask before the acid is admitted to contact with the other reagents. Potassium iodide (3 grm.) and water (200 c.m.^{3}) were put into the receiver C, and a little of this solution was allowed to flow into the trap *g*. Ammonium molybdate carefully weighed (0·3 grm.) and potassium iodide (0·5 grm. to 0·75 grm.) were introduced into the distillation-flask B, the apparatus was connected as shown in the figure and carbon dioxide was passed freely through the whole apparatus for some minutes. The stop-cock *d*, between the bulb of the funnel A and the flask B, was closed and hydrochloric acid (40 c.m.^{3}, sp. gr. 1·12) was poured into the funnel; the air above the liquid in the funnel was displaced by carbon dioxide through the space between the neck of the funnel and the loosely adjusted stopper carrying the inlet tube; the connection between the funnel and inlet tube was tightened, the stop-cock opened, and the acid, under the pressure of carbon dioxide, was permitted to flow into the flask. In this way the acid, iodide, and molybdate were made to interact with little danger of the presence of oxygen. The flask was heated by the Bunsen burner and the iodine evolved, passing over quietly in the slow current of carbon dioxide, collected in the receiver. The liquid was boiled until fumes of iodine were no longer visible above the liquid in the flask and connecting tubes backed by a ground of white, and then a full minute more. At this stage, the green colour of the liquid having developed fully, the apparatus was permitted to cool, the current of carbon dioxide was increased, the cap of the receiver was loosened at *f*, the contents of the trap were washed back into the receiver, the rest of the apparatus was lifted bodily from the receiver, the liquid adhering to the inlet tube was washed off into the receiver, and the end of the tube was dipped immediately into a solution of potassium iodide. The constant flow of carbon dioxide prevented reflux of air during the transfer, and as soon as the end of the tube had been submerged in the solution of potassium iodide (which was employed not only as a water-seal, but to catch any iodine still carried in the gas), it was possible to reduce the rapidity of the current.

After titrating the iodine in the distillate the receiver was again placed in the train and the process of distillation was resumed under the former conditions and continued until the volume of the liquid, as indicated upon the scale, had diminished to 25 c.m.^{3}, when the distillation was interrupted. The apparatus was manipulated as before to prevent access of air, and the iodine evolved in the second treatment determined. A third period of distillation served to show the iodine liberated during the concentration of the liquid from 25 c.m.^{3} to 10 c.m.^{3}

(To be continued).

MISCELLANEOUS.

Salts of Pertungstic and Permolybdic Acids.—P. Melikoff and L. Pissarjewsky.—To prepare these salts solutions of sodium and potassium hypotungstates and hypomolybdates are cooled to −2°, and added to the calculated quantity of H_2O_2; on addition of alcohol cooled to −12°, precipitation takes place. The precipitate is kept for some time at −12°, and then filtered and washed with alcohol. It can then be dried on a porous tile and analysed. The salts prepared by this method have the following compositions:—

$$Na_2O_2.WO_4.H_2O_2+(Na_2O_2)_2WO_4+7H_2O$$
$$Na_2O_2.WO_4.H_2O_2$$
$$K_2O_4.WO_4.H_2O$$
$$K_2O_2.MoO_3.H_2O_2.$$

All these salts are very unstable, and are decomposed by water, with evolution of oxygen. To analyse the salts a weighed quantity of the salt is decomposed by dilute H_2SO_4 at −6°, and the liberated oxygen titrated with permanganate solution.—*Ber. der Deutsch. Chem. Gesell.*, 1898, No. 6.

MEETINGS FOR THE WEEK.

Friday, 28th.—Physical, 5. "An Influence Machine," by W. R. Pidgeon, M.A. "The Repetition of an Experiment on the Magneto-optic Phenomenon Discovered by Righi," by Prof. Silvanus P. Thompson, F.R.S. "The Magnetic Fluxes in Meters and other Electrical Instruments," by Albert Campbell, B.A.

THE CHEMICAL NEWS.

Vol. LXXVIII., No. 2031.

NOTE ON THE INTERACTION OF SODIUM ARSENITE AND SODIUM THIOSULPHATE.*

By L. W. McCAY.

In the Chemical News for March 25th, 1898 (vol. lxxvii., p. 131), there is a note by Dr. Leonard Dobbin in which he calls attention to a new and interesting reaction which takes place when concentrated aqueous solutions of a cyanide and a thiosulphate are mixed and allowed to stand. The products formed are a thiocyanate and a sulphite :—

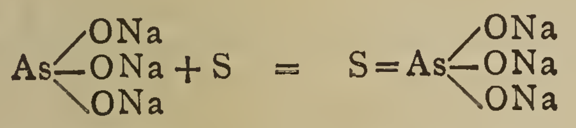
$$KCN + K_2S_2O_3 = CNSK + K_2SO_3.$$

This reaction of Dr. Dobbin is in some respects similar to one I discovered in the summer of 1897. By means of my reaction I have been able to prepare the tertiary sodium salt of orthomonothioxyarsenic acid in large amounts and in beautiful well-defined crystals.

I simply rub up in a mortar, with a sufficient quantity of caustic soda solution to form a thick paste, the calculated amounts of sodium arsenite and sodium thiosulphate. The reaction proceeds as follows :—

$$Na_3AsO_3 + Na_2S_2O_3 = Na_3AsO_3S + Na_2SO_3.$$

An atom of sulphur leaves the thiosulphate molecule and attaches itself *directly* to the arsenic atom of the arsenite molecule (*Chemiker Zeitung*, 1896, xx., No. 75) :—

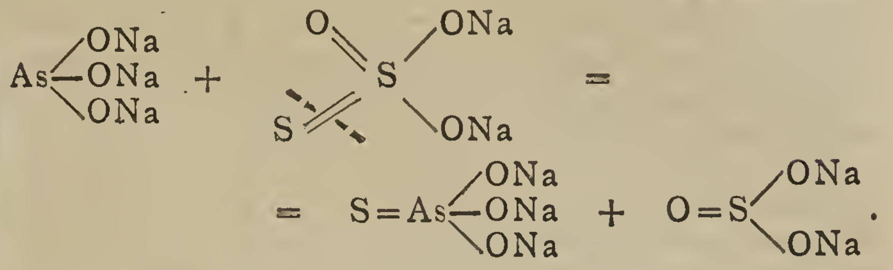


The paste is dissolved in water, the solution filtered, and from the filtrate the salt obtained by crystallisation. It is readily purified by one or two subsequent crystallisations from water.

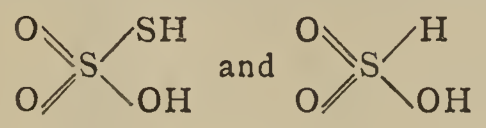
	Calculated for $Na_3AsO_3S + 12H_2O$.	Found for $Na_3AsO_3S + 12H_2O$.
Na_3	15·70 per cent	15·94 per cent
S	7·28 „	7·30 „
As	17·05 „	17·06 „

It may be well to state, however, that I am not in the habit of making use of this reaction for preparing the orthomonothioxyarseniates. The sodium compound is most easily and rapidly obtained by rubbing up in a mortar, with enough water to form a paste, the stöchiometrical amounts of *sulphur*, caustic soda, and arsenious oxide, dissolving the resulting mass in water, filtering the solution, concentrating it, and allowing the salt to crystallise out. A few c.c. of absolute alcohol added to the contents of the mortar serve to accelerate the reaction in a very marked manner. It will be seen that this latter method is but a modification of that of Weinland and Rumpf. It is, however, simpler and quicker than their original method, and, as far as yield is concerned, leaves nothing to be desired.

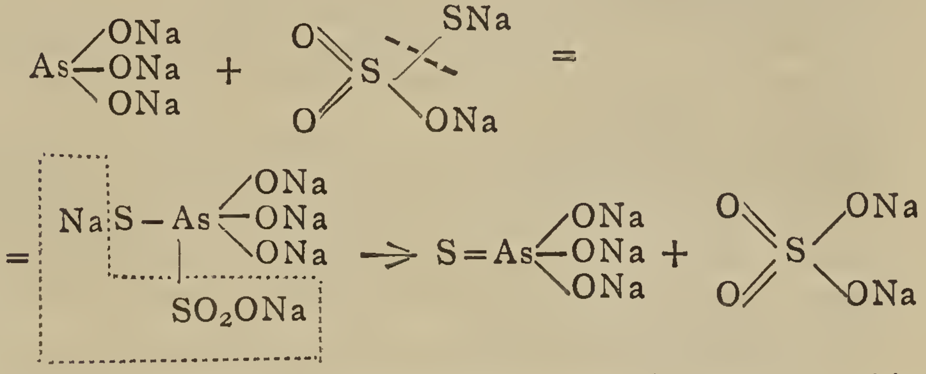
It was this method for preparing $Na_3AsO_3S + 12H_2O$ which suggested to me the use of sodium thiosulphate. As is well known, $Na_2S_2O_3$ yields sulphur very readily, especially when used for fusion purposes. The mechanism of the reaction is undoubtedly complicated. The simplest interpretation would be this :—



Since, however, the reactions of organic chemistry point to—



as representing the constitutions of thiosulphuric and sulphurous acids, such a simple interpretation cannot be held. If we assume the momentary existence of a complex intermediate compound, the reaction might be represented in this way :—



I am indebted to my friend Mr. Fred Neher for this suggestion.

Princeton, New Jersey, U.S.A.

ACTION OF WATER ON METALLIC COPPER AND LEAD.

By ROBERT MELDRUM, F.C.S.

Action on Copper.

The results obtained are expressed in parts per 100,000. The experiments were made in large test-tubes, each containing 100 c.c. of water and 7 feet bright copper wire 1/16″ diameter. The metal dissolved was estimated by the potassium ferrocyanide colorimetric method.

1. Lake water containing 26·06 total solids; 0·0056 free NH_3; 0·0126 albumenoid NH_3; 1·756 Cl; in 24 hours dissolved 0·099 Cu.
2. Water containing 27·66 total solids; no free NH_3; 0·001 albumenoid NH_3; 1·22 Cl; dissolved in 24 hours 0·023 Cu.
3. Town water supply, 21·77 total solids; 0·55 SiO_2; 0·03Al_2O_3·P_2O_3; 4·70 $CaSO_4$; 10·50 $CaCO_3$; 0·92 $MgCO_3$; 2·07 NaCl; 3·0 organic matter; after 94 hours contact dissolved 0·0825 Cu.
4. Free NH_3 water, and, therefore, free CO_2, after 115 hours contact contained 0·1925 Cu. By this time the water had absorbed both NH_3 and CO_2.
5. Distilled water in five months dissolved 0·055 Cu.
6. The following is the analysis of a sludge from a water tube boiler after being in use for some years. It is interesting as indicating a constant solvent action of the water on the copper and brass fittings :—H_2O, 13·12 per cent; SiO_2, 2·4 per cent; Fe_2O_3·Al_2O_3, 2·30 per cent; $CaCO_3$, 81·90 per cent; copper, 0·006 per cent.

Action on Lead.

These experiments were made with six different lengths of new lead piping, 2′ long × ½″ bore, cut from the same coil and closed at one end, each of which is distinguished by a number placed before the lead determination. These were treated by frequently filling and agitating with their respective waters during 24 hours, so as to corrode the

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* Received August 2, 1898.

bright surfaces as much as possible. The two standard solutions used were prepared by dissolving 0·2 grm. of piping in acetic acid, and making up to 1000 c.c. with each water. Water A had a hardness of 3·5° before boiling and 3·2° after, and yielded a total residue of 8·5. Water B had a hardness of 18·6° before and 5° after boiling, and gave a total residue of 19·28. The former had a constant solvent action on lead while in practical use, whereas B had no action. Results are expressed in parts per 100,000.

	A.	B.
Pb dissolved in ¼ hour ..	1. 0·99	—
„ „ ½ „ ..	2. 2·38	—
„ „ 1 „ ..	3. 3·37	4. 0·021
„ „ 4 hours ..	1. 3·97	5. 0·049
„ „ 21 „ ..	2. 2·98	6. 0·099
„ „ 120 „ ..	3. 2·38	—

Here we see that the solvent power of A is 160, 81, and 30 times greater than B.

The pipes were washed, and filled with water charged with about 20 c.c. of CO_2 per pint, and in one hour A dissolved (1) 3·37 and B (4) 0·021, the same as the waters dissolved without gas.

Water A was almost saturated with CO_2, and dissolved in half an hour (2) 0·99, in one and a half hours (2) 5·96.

A saturated with CO_2, then agitated with precipitated $CaCO_3$, allowed to settle, and decanted clear unfiltered liquor into pipes, contained in one hour (3) 0·238; another experiment gave only trace.

Pint of A, mixed with 10 c.c. of saturated CaO solution, and allowed to settle for one hour, when the water gave faint alkaline reaction, thus showing slight excess of CaO, whereas the decanted clear liquid dissolved only a trace in one hour. Another experiment, but with the water heated after addition of CaO, dissolved 0·061.

When water A was thoroughly agitated with precipitated $CaCO_3$, and *filtered*, it did not dissolve any lead. Filtered through 3″ of ¼″ pieces of washed marble, at the rate of half a pint per minute, dissolved no lead after seventy minutes contact.

AN EXAMINATION OF THE PRODUCTS OBTAINED BY THE DRY DISTILLATION OF BRAN WITH LIME.[*]

By W. F. LAYCOCK, Ph.D.

The Distillation.

Twenty-two kilos. of wheat bran mixed with 44 kilos. of burnt lime were distilled in a large iron retort over a coal fire. The products of distillation passed over a large T-tube which was opened from time to time to draw off the distillate. The more volatile portion was led through a condenser having a worm 7 metres long placed in a tank filled with cold water.

Soon after applying heat to the retort, dense white fumes made their appearance in the receiver and continued to be evolved until the whole of the bran had been decomposed. The fumes had a strong characteristic smell. On ignition the escaping gases burnt with a pale luminous flame. The distillation proceeded quietly, and was finished in about seven hours. The residue in the retort was a grey mass containing particles of charcoal. The distillate consisted of a red-brown aqueous solution, with a black oil on its surface. The solution A was separated from the oil B.

Examination of A.

The aqueous solution, after filtering, measured 9·6 litres and weighed 9·7 kilos. It smelled of herring brine, and was strongly alkaline. On distilling a small quantity, crystals—which proved to be ammonium bicarbonate—were formed in the condenser. When a portion was acidified with hydrochloric acid, carbon dioxide was evolved, and a pine-splinter boiled in the liquid gave a brilliant pyrrol-reaction. The whole of the solution, together with 100 grms. of solid caustic potash, was placed in a large can and distilled with steam. When the distillate ceased to give the pyrrol-reaction the distillation was discontinued. On extracting the alkaline solution remaining in the still with ether, drying the extract with potassium carbonate and distilling, about 6 grms. of reddish-yellow oil (1) boiling at 190—310°[*] were obtained. The oil contained homologues of pyrrol, and gave on analysis 11 per cent nitrogen.

The Distillate from the Steam Distillation.—This weighed 1650 grms. It was a yellow aqueous solution, with a small quantity of oil on its surface. The oil was separated by fitration, dried, and distilled. About 3 grms. of oil (2) boiling at 130—240°, containing pyrrols and yielding 9 per cent nitrogen, distilled over.

The aqueous filtrate[†] was neutralised with hydrochloric acid, made slightly acid, and distilled with steam. The distillate, 1·5 litres, was distilled on the water-bath. About 77 grms. of a colourless oil passed over. The solution remaining in the distilling flask was saturated with potassium carbonate and extracted with ether. The extract yielded 15 grms. of an oil (3) boiling between 70—200°, and containing pyrrols and 11·5 per cent nitrogen.

The 77 grms. of colourless oil were distilled, 29 grms. (4) passing over between 62—90°. When the temperature reached 90° the liquid in the distilling flask suddenly became turbid and separated into an aqueous and an oily layer. The distillation was stopped at this point and the oily layer extracted with ether. About 2 grms. of colourless oil (5) boiling at 120—180° were obtained. This oil also contained pyrrols, and gave on analysis 12 per cent nitrogen.

The oils (1), (2), (3), *and* (5), *amounting to* 26 *grms.*, averaging about 11 per cent nitrogen and boiling between 70—310°, were mixed. Repeated attempts to isolate the pyrrols, and obtain fractions of constant boiling-point, failed owing to the presence of hydrocarbons and bases. The mixture was boiled for some time with hydrochloric acid to convert the pyrrols into pyrrol-red, and thus ascertain approximately their amount. On filtering the liquid 16 grms. of pyrrol-red were obtained.

The 29 *grms. of oil* (4) *boiling* 62—90° gave the following reactions:—The oil had a sweet smell. On shaking sodium bisulphite with it, no crystals separated, proving the absence of acetone. Ammoniacal silver nitrate, Fehling's solution, and a solution of magenta decolourised by sulphurous acid were not altered, consequently aldehyds were absent.

A portion treated with phenylhydrazine became warm and quite turbid, proving the presence of a ketone.

From 6 grms. of oil 2 grms. of a hydrazone were separated. On distilling this orange-red liquid hydrazone, it decomposed suddenly at about 90°. It behaved similarly under reduced pressure (420 m.m.) at about 80°.

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[*] This investigation was carried out in the Laboratory of Prof. L. Knorr, at the University of Jena,

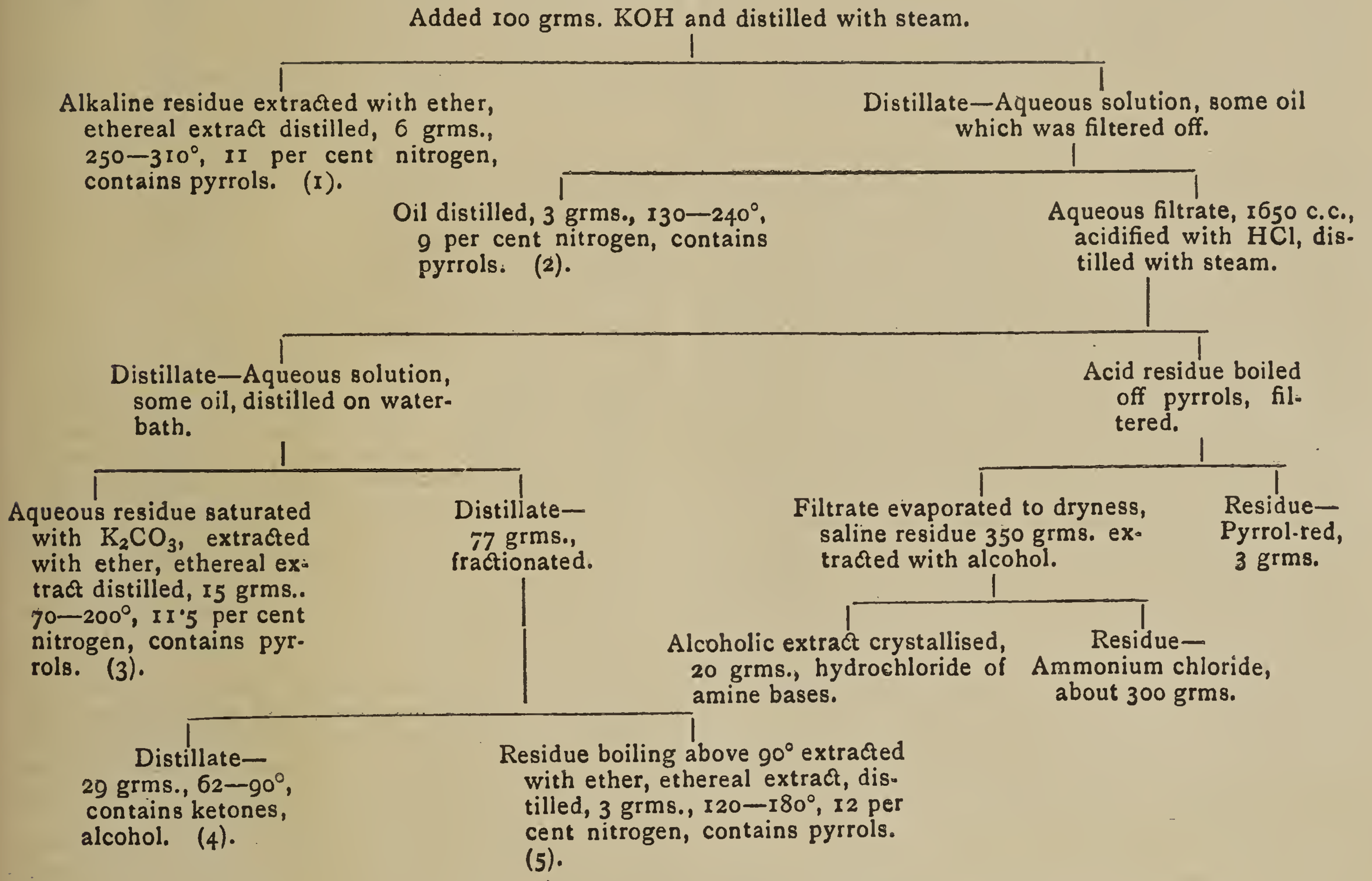
[*] *Colour Reactions with Pine-splinters.*—As the last drop passing over at 310° imparted a bright red colour to a pine-splinter on boiling with dilute hydrochloric acid, an indole is probably present. A pine-splinter dipped in an emulsion of water and the oil formerly termed "metacetone," becomes, on exposure to the vapour of hydrochloric acid, violet-blue. "Metacetone" consists chiefly of dimethyl furfurane mixed with a hydrocarbon (*Ber.*, xxii., 103). A pine-splinter simply boiled in water and exposed to hydrochloric acid vapour becomes emerald-green. It is probable that some pine-splinter reactions mentioned in chemical literature have been masked by the latter. Furfurane has been stated to give, under similar conditions, a green colour (*Ber.*, xx., Ref. 221).

[†] The filtrate gave the following reactions:—On adding potassium carbonate, ammonia and amines were evolved and an oil separated out. On extracting the latter with ether and evaporating, a small quantity of a very pungent smelling oil remained. On adding water and bringing a rod moistened with hydrochloric acid near it, white fumes were produced, showing the presence of organic bases. A solution of magenta decolourised by sulphurous acid was not affected, proving that aldehyds were absent.

TABLE I.

			Melting-point.	Calculated for—	Melting-point.
0·2017 grm. Pt salt on ignition gave	0·0832 grm. Pt	= 41·25 per cent	228°	$(CH_3NH_2HCl)_2PtCl_4$. 41·19 per cent	
0·1131 ,, ,, ,,	0·0472 ,, ,,	= 41·73 ,,	230°		
0·0969 ,, ,, ,,	0·0384 ,, ,,	= 39·62 ,,	223°	$(C_2H_5NH_2HCl)_2PtCl_4$. 38·09 per cent	219°
0·0956 ,, ,, ,,	0·0366 ,, ,,	= 38·28 ,,	223°		
0·2087 ,, ,, ,,	0·0775 ,, ,,	= 37·13 ,,	228°	$(CH_3)_3N.HCl)_2PtCl4$. 36·81 per cent	240—245°
0·1178 ,, ,, ,,	0·0436 ,, ,,	= 37·01 ,,	237°		Decomposes.

TABLE II.—THE AQUEOUS SOLUTION A, 9·7 kilos.



Added 100 grms. KOH and distilled with steam.

Alkaline residue extracted with ether, ethereal extract distilled, 6 grms., 250—310°, 11 per cent nitrogen, contains pyrrols. (1).

Distillate—Aqueous solution, some oil which was filtered off.

Oil distilled, 3 grms., 130—240°, 9 per cent nitrogen, contains pyrrols. (2).

Aqueous filtrate, 1650 c.c., acidified with HCl, distilled with steam.

Distillate—Aqueous solution, some oil, distilled on water-bath.

Acid residue boiled off pyrrols, filtered.

Aqueous residue saturated with K_2CO_3, extracted with ether, ethereal extract distilled, 15 grms.. 70—200°, 11·5 per cent nitrogen, contains pyrrols. (3).

Distillate—77 grms., fractionated.

Filtrate evaporated to dryness, saline residue 350 grms. extracted with alcohol.

Residue—Pyrrol-red, 3 grms.

Alcoholic extract crystallised, 20 grms., hydrochloride of amine bases.

Residue—Ammonium chloride, about 300 grms.

Distillate—29 grms., 62—90°, contains ketones, alcohol. (4).

Residue boiling above 90° extracted with ether, ethereal extract, distilled, 3 grms., 120—180°, 12 per cent nitrogen, contains pyrrols. (5).

On adding two or three drops of the oil to 1 c.c. of a freshly prepared half per cent solution of sodium nitroprusside, making up to 3 c.c. with water, and adding dilute caustic potash (1·14) until, just alkaline, a deep red colouration was produced. The colour turned violet-red on acidifying with acetic acid, proving methylpropyl ketone to be present (Béla von Bittó, *Ann. Chem. Pharm.*, 267, 372).

On warming the oil with glacial acetic acid, the smell of acetic ether was noticed. When iodine was dissolved in the oil, and sodium carbonate solntion added, and the mixture heated to 70° until decolourised, the characteristic smell of iodoform was observed. On cooling, the solution deposited yellow crystals of iodoform. These tests show the presence of ethyl alcohol.

Sodium acted violently on the oil, hydrogen being evolved, and a yellow amorphous mass remained. The liquid smelled of pyridine bases.

The oil contained 3·85 per cent nitrogen. The pine splinter reaction with hydrochloric acid was violet, demonstrating the presence of a furfuran homologue.

The Acid Residue from the Steam Distillation.—This was made strongly acid with hydrochloric acid, and boiled in a large basin for six hours, water being added occasionally. The pyrrols were thus volatilised or decomposed. After filtering off 3 grms. of pyrrol-red the solution was evaporated to dryness on the water-bath. About 350 grms. of a dark crystalline mass remained. This substance was purified by boiling with animal charcoal, filtering, and crystallising. The crystals of ammonium chloride obtained were extracted with alcohol, the alcoholic extract and the aqueous mother-liquor being eventually mixed and evaporated to dryness. The salts thus obtained were further purified by distillation with solid caustic potash, the vapours being absorbed in hydrochloric acid, and the resulting salts subjected to fractional crystallisation. Eventually three portions, almost free from ammonium chloride, were obtained, viz., 1 grm. of shining deliquescent plates, 2 grms. of long needles, and 17 grms. of uncrystallisable mother-liquor containing deliquescent needles.

Each fraction gave similar reactions. On boiling a portion with potash solution, a strong smell of herring-brine was produced, and the evolved gases burnt on ignition.

On boiling with chloroform and alcoholic potash, primary amines were detected by the characteristic smell of the carbamine evolved.

Portions of the different fractions were separately treated with platinum tetrachloride, and the resulting platinum salts dissolved in water and re-crystallised or precipitated with alcohol. A series of platinum compounds differing in crystalline form, melting-point, and constitution was the result, but owing to the small amount of substance at disposal a more complete separation was not attempted. A number of analyses were made, and the results appear to agree fairly with well with known salts. (See Table I.).

Each of the above platinum salts decomposed on melting.

From these figures it is evident that methylamine, ethylamine, and trimethylamine formed part of the mixed salts.

(To be continued).

The Chemical Laboratory,
46, Boar Lane, Leeds.

THE IODOMETRIC DETERMINATION OF MOLYBDENUM.[*]

By F. A. GOOCH and JOHN T. NORTON, Jun.

(Concluded from p. 208).

During the first period of distillation the liquid assumed the clear green colour, which changed but slightly until the beginning of the third period, when the tint verged upon olive, and at the end of the operation the colour of the liquid was an olive brown which grew browner on cooling. The addition of considerable hydrochloric acid to the residual liquid restored the clear green colour, while water changed the olive brown to reddish yellow, the tint varying with the dilution. The results of these experiments are recorded in 1 to 5 of the accompanying table. In division A are given the weights of molybdenum trioxide corresponding to the amounts of iodine found in the three stages of distillation; in division B, the molybdenum trioxide corresponding to the iodine evolved from the beginning of the process to the end of each stage.

The mean error of the indications taken during the period of distillation advocated by Friedheim and Euler is 0·0045 grm.—;[†] that of the period of concentration from 40 c.m.^{3} to 25 c.m.^{3} is 0·0008 grm.+; and that of the full period of distillation is 0·0014+. It is plain beyond a peradventure that in the process as conducted by Friedheim and Euler, excepting the protection against atmospheric action, the theoretical reduction of the molybdic acid does not take place. The best results are obtained when the distillation is prolonged until the original volume of 40 c.m.^{3} has been diminished to 25 c.m.^{3}. Concentration beyond the limit of 25 c.m.^{3} tends to develop a tendency toward over-reduction, especially when the amount of potassium iodide is increased beyond about 0·5 grm. in excess of that theoretically required. This is shown in Experiments 6 and 7, conducted otherwise similarly to those described above, in which the amount of potassium iodide was increased to 1 grm. and 2 grms. The error after distilling from 40 c.m.^{3} to 10 c.m.^{3}, the lowest limit of the preceding experiments, was 0·0053 grm.+ and 0·0040 grm.+, and the latter error was increased to 0·0074 grm.+ on repeating the distillation with a fresh portion (30 c.m.^{3}) of the acid. It is interesting to note incidentally that in the experiment in which the largest amount of iodide (2 grms.) was used the solution did not take the green colour at any stage of the distillation, probably because the large excess of iodide held the free iodine and so masked the colour until the degree of concentration was reached at which the olive-brown colour displaces the green.

The possibility of the interaction of atmospheric oxygen and gaseous hydriodic in the analytical process, even to the extent of producing errors of from 1 to 3 per cent reckoned as molybdenum trioxide, was recognised by Friedheim and Euler; and it was to obviate this difficulty that the recommendation was made by them to warm very gradually the distillation flask filled two-thirds with the mixture of iodide, molybdate, and acid, and to raise the liquid to actual boiling only when the space above the liquid in the retort and in the connecting tube is filled as completely as possible with iodine vapour, while the liquid in the receiver begins to rise in the tube.

A.

	HCl (sp. g. 1·12) taken.	KI in retort.	MoO_3 taken as ammonium molybdate.	MoO_3 corresponding to iodine found. 1st Stage.—40 c.m.^{3} to 32 c.m.^{3}, Green colour.	MoO_3 corresponding to iodine found. 2nd Stage.—32 c.m.^{3} to 25 c.m.^{3}.	MoO_3 corresponding to iodine found. 3rd Stage.—25 c.m.^{3} to 10 c.m.^{3}.
	C.m.^{6}.	Grm.	Grm.	Grm.	Grm.	Grm.
1.	40	0·5	0·2455	0·2399	0·0076	0·0004
2.	40	0·5	0·2455	0·2402	0·0053	0·0013
3.	40	0·5	0·2455	0·2414	0·0040	0·0004
4.	40	0·75	0·2455	0·2404	0·0061	0·0004
5.	40	0·75	0·2455	0·2431	0·0037	0·0004
6.	40	1·	0·2455	0·2404	0·0085	0·0019
7.	50	2·	0·2455	—	—	—

B.

	MoO_3 corresponding to iodine found during period of Friedheim and Euler. (1st stage).	Error.	MoO_3 corresponding to iodine found in concentrating from 40 c.m.^{3} to 25 c.m.^{3}.	Error.	MoO_3 corresponding to iodine found in concentrating from 40 c.m.^{3} to 10 c.m.^{3}.	Error.
	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
1.	0·2399	0·0056—	0·2475	0·0020+	0·2479	0·0024+
2.	0·2402	0·0053—	0·2455	0·0000	0·2468	0·0013+
3.	0·2414	0·0041—	0·2454	0·0001—	0·2458	0·0003+
4.	0·2404	0·0051—	0·2465	0·0010+	0·2469	0·0014+
5.	0·2431	0·0024—	0·2468	0·0013+	0·2472	0·0017+
6.	0·2404	0·0051—	0·2489	0·0034+	0·2508	0·0053+
7.	—	—	—	—	0·2495 0·2529*	0·0040+ 0·0074+

* On repeating distillation with a fresh charge of acid.

The action of atmospheric oxygen upon the solution of hydriodic acid must, however, be also taken into account. It is a familiar fact that when a considerable excess of strong hydrochloric acid is allowed to act in contact with air upon potassium iodide (free from iodate) dissolved in a little water, the mixture is coloured by free iodine. The amount of iodine liberated by atmospheric action is insignificant when the acid is very dilute, but is considerable when the acid is strong, and increases with time and rise in temperature, as shown in the experiments recorded in the accompanying table.

KI taken.	Volume.	Percentage of HCl in aqueous acid.	Time in minutes.	Temperature, Centigrade.	MoO_3 equivalent to iodine found.	Remarks.
Grm	C.m.^{3}.				Grm.	
-	166	2	1	23°	none	
1	66	2	10	23°	0·0001	
1	66	24*	10	23°	0·0017	Diluted to 500 c.m.^{3} before titrating with $Na_2S_2O_3$.
1	66	24*	4	From 23° to the boiling point.	0·0067	
1	66	24*	10		0·0121	

* This corresponds nearly to sp. gr. 1·12.

Even the precaution to conduct the operation in an atmosphere of carbon dioxide does not eliminate all chance of error of this sort unless the liquid of the mixture —the hydrochloric acid—is free from air. The experi-

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[*] Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, vol. vi., 1898.

[†] Even this figure does not disclose the full error, which is partly counterbalanced, as will appear later, by the effect of oxygen dissolved in the acid used in the process.

ments of the following statement, which were conducted in the apparatus and manner previously described, show this point clearly. Thus, 40 c.m.³ of unboiled acid, sp. gr. 1·12, introduced enough air into the apparatus to cause an error of 0·0013 grm., reckoned in terms of molybdenum trioxide, while the iodine set free by the action of the residual acid of this experiment upon another grm. of potassium iodide introduced without admission of air corresponded to only 0·0002 grm. in terms of molybdenum trioxide. The use of acid of sp. gr. 1·1, freshly boiled in the air, obviously reduces the error due to the unboiled acid, but even in this case the effect of included oxygen was not wholly obviated.

KI taken.	Volume.	Percentage of HCl in aqueous acid.	Concentration by boiling.	MoO_3 equivalent to iodine found.	Remarks.
Grm.	C.m.³.		C.m.³.	Grm.	
1	40	24	40—30	0·0013	Iodine determined in distillate.
			30—20	0·0002	1 grm. of KI added to retort at the beginning of the 2nd stage.
1	40	20	40—25	0·0005	The acid taken, sp. gr. 1·1, was freshly boiled and introduced at once upon KI in retort in CO_2.

It is obvious that the procedure recommended by Friedheim and Euler can by no possibility eliminate the effect of atmospheric action upon the mixture of acid and iodide. The extent of such action must depend upon such conditions as the size of the apparatus, the time of exposure, the body of air above and dissolved in the liquid, and the rate of displacement of the air. How great the error due to atmospheric action actually was in the process as conducted by Friedheim and Euler we, of course, have no means of knowing. It is to be hoped, however, that it was sufficiently great to counterbalance that other inevitable error (of about 5 m.grms.) which exists by reason of the incompleteness with which molybdic acid is reduced under the conditions which these investigators prescribe; for the value of Euler's work upon the vanadiomolybdates rests upon the chance that these two very considerable and indisputable tendencies to error may have neutralised one another.

It has been shown clearly that our former criticism of the procedure of Friedheim and Euler is justified in every particular. We have no change to make in the recommendation made therein as to necessary modifications.

If the conditions seem difficult, there is an alternative in the method proposed in the former article (*Am. Journ. Sci.*, IV., ii., 156), according to which the molybdate is reduced by the acid and iodide in an Erlenmeyer beaker (trapped loosely by means of a short bulbed tube hung in the neck), and the molybdenum pentoxide, freed from iodine by boiling, is reoxidised by standard iodine in alkaline solution.

ON THE DETECTION OF SULPHIDES, SULPHATES, SULPHITES, AND THIOSULPHATES, IN THE PRESENCE OF EACH OTHER.*

By PHILIP E. BROWNING and ERNEST HOWE.

Some three years ago R. Greig Smith (Chemical News, vol. lxxii., 39) published a method for the detection of sulphates, sulphites, and thiosulphates in the presence of each other, which promised much toward the solution of this most difficult problem. The method may best be described in the author's own language:—To a solution of the salts of the above-mentioned acids "barium chloride is added in excess, together with a good quantity of ammonium chloride, which, like many salts of ammonium, potassium, and calcium, acts as a flocculent or coagulant, and facilitates the filtration of the barium sulphate. Hydrochloric acid is next added, drop by drop, until it is evident that there is no further solution of barium sulphite and thiosulphate, and that only the sulphate remains undissolved; the solution is then filtered through a moistened double filter-paper, which should be free from 'pin holes.' The filtrate will probably be clear, but if not it should be returned to the filter for a second filtration. When too much thiosulphuric acid is present, the clear filtrate will visibly become clouded, or from being whitish will become more opaque; if this occurs the solution should be thrown out, and a fresh portion made more dilute. A solution of iodine is added to half of the filtrate until the colour is of a permanent yellow tinge; a white precipitate indicates the presence of a sulphite which has been oxidised by the iodine to sulphate. In the absence of a decided precipitate traces of sulphite may easily be detected by comparing the treated and untreated halves of the filtrate—a procedure which very often saves a good deal of time, as it is unnecessary to wait until a clear filtrate is obtained. The two halves are mixed, and if the yellow colour disappears more iodine is added, the solution filtered, and the filtrate divided into two halves as before. With a slight turbidity filtration may be omitted. Bromine water is added to one of the halves when any thiosulphate in the original solution shows itself as a white precipitate of barium sulphate, readily seen on comparing the two test-tubes. The thiosulphate is by iodine converted to tetrathionate, which is oxidised by bromine water to sulphate." Three objections to this method as described will readily occur to the reader: first, the readiness with which the thiosulphate is decomposed by free hydrochloric acid; second, the comparatively large amount of acid necessary to effect the complete solution of the barium sulphite and thiosulphate when precipitated with the sulphate as compared with the amount required to prevent the precipitation; third, the lack of delicacy necessitated by a comparison of portions of a coloured solution in looking for small precipitates. The work to be described was undertaken to overcome these difficulties and to test the accuracy of a modified method. Solutions of potassium sulphite and sodium thiosulphate were made approximately decinormal and standardised in the usual manner against an iodine solution of known value. It was found that by making a solution containing sulphates, sulphites, and thiosulphates very faintly acid, the sulphates and thiosulphates were held completely in solution when the barium sulphate was precipitated. The extreme sensitiveness of a thiosulphate to the decomposing action of free hydrochloric acid suggested the possible substitution of acetic acid to hold the sulphites and thiosulphates in solution. This being a weaker acid, we hoped to avoid the decomposition of the thiosulphate into sulphur and sulphurous acid, or at least to delay the decomposing action. The results of these experiments appear in Table I.

From these results it would seem that the decomposition of a thiosulphate is more rapid in presence of hydrochloric acid than in presence of a much larger amount of acetic acid.

Our next experiments were directed toward a determination of the effect of adding stannous chloride to bleach the colour of the free iodine and bromine used in the oxidation and of acidifying with acetic acid, before treating with barium chloride. That is to say, the process as we used it consisted in acidifying the solution to be tested with acetic acid, adding barium chloride, filtering to remove precipitated sulphate (always present in the

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[*] Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, vol. vi., Oct., 1898.

TABLE I.

	Volume c.m.³ of water.	Hydrochloric acid (1 : 4). Drops.	Acetic acid. Drops.	$Na_2S_2O_3$ taken. Grm.
1.	10	2	—	0·01 (*a*)
2.	10	2	—	0·1 (*b*)
3.	100	3	—	0·1 (*c*)
4.	10	—	8	0·01 (*d*)
5.	10	—	8	0·1 (*e*)
6.	100	—	10	0·1 (*f*)
7.	100	—	10	0·25 (*g*)
8.	100	—	10	0·5 (*h*)
9.	100	—	10	1·0 (*i*)

Result.

(*a*) No sulphur in 20 minutes.
(*b*) Sulphur in 45 seconds.
(*c*) Sulphur in 15 minutes.
(*d*) No sulphur in 20 minutes.
(*e*) Sulphur in 90 seconds.
(*f*) No sulphur in 20 minutes.
(*g*) Sulphur in 15 minutes,
(*h*) Sulphur in 60 seconds.
(*i*) Sulphur in 30 seconds.

TABLE II.

	K_2SO_3 taken. Grm.	Volume of water. C.m.³.	$BaSO_4$ precipitated after oxidation with iodine.
1.	0·1	10	Very abundant (*a*)
2.	0·01	10	Abundant (*b*)
3.	0·001	10	Distinct (*c*)
4.	0·0005	10	Fair (*d*)
5.	0·0001	10	Faint (*e*)

Remarks.

(*a*) Plainly visible before adding $SnCl_2$.
(*b*) Plainly visible before adding $SnCl_2$.
(*c*) More distinct after adding $SnCl_2$.
(*d*) Hardly visible before adding $SnCl_2$.
(*e*) Invisible before adding $SnCl_2$.

TABLE III.

	$Na_2S_2O_3$ taken. Grm.	Volume of water. C.m.³	$BaSO_4$ precipitated by action of iodine.	$BaSO_4$ precipitated by action of bromine.
			A.	
1.	0·1	10	Distinct	Abundant (*a*)
2.	0·01	10	Faint	Abundant (*b*)
3.	0·001	10	None	Distinct (*c*)
4.	0·0005	10	None	Faint (*d*)
5.	0·0001	10	None	Very faint (*e*)

Remarks.

(*a*) Sulphur separated in 30 seconds.
(*b*) No sulphur in 90 seconds.
(*c*) No sulphur in several minutes.
(*d*) No sulphur; $SnCl_2$ necessary.
(*e*) No sulphur; $SnCl_2$ necessary.

B.

	$Na_2S_2O_3$ taken. Grm.	Volume of water. C.m.³	$BaSO_4$ precipitated by action of iodine.	$BaSO_4$ precipitated by action of bromine.
1.	0·1	10	Faint	Abundant (*a*)
2.	0·01	10	None	Abundant (*b*)
3.	0·001	10	None	Distinct (*c*)
4.	0·0005	10	None	Faint (*d*)
5.	0·0001	10	None	Very faint (*e*)

Remarks.

(*a*) No sulphur separated in 1 minute.
(*b*) No sulphur separated in several minutes.
(*c*) No sulphur.
(*d*) No sulphur; $SnCl_2$ necessary.
(*e*) No sulphur; $SnCl_2$ necessary.

sulphite), adding iodine to the filtrate until the colour was permanent, bleaching with stannous chloride, filtering off the sulphate which represents the sulphite originally present, adding bromine in excess to the filtrate, and again bleaching with stannous chloride to increase the visibility of the sulphate which now represents the thiosulphate originally present. The details of experiments in which the sulphite was taken alone and oxidised with iodine are given in Table II.

A corresponding series of experiments was made in which hydrochloric acid was substituted for acetic acid, and essentially the same results were obtained.

A similar series of experiments was made to test the effect of treating the thiosulphate in an acidified solution, first with iodine and then after filtration (if a precipitate had formed) with bromine. In the experiments of division A hydrochloric acid (a few drops) was added before treating with barium chloride, and in those of division B acetic acid was used similarly. Stannous chloride was employed to bleach the excess of iodine and bromine. (See Table III.).

From these experiments the advantage of the use of acetic acid becomes apparent, as does also the use of stannous chloride in increasing the delicacy of this indication, so that a small fraction of a milligramme may easily be detected.

If relatively large amounts of thiosulphate are present with small amounts of sulphite, we have sometimes found it advantageous to manipulate so that even the slow decomposition of the thiosulphate by acetic acid may be avoided by first attempting precipitation with barium chloride in a dilute ammoniacal solution. By this method the barium sulphate and sulphite are separated from the thiosulphate and identified—the sulphate by its insolubility in dilute hydrochloric acid, and the sulphite by the action of iodine upon the acid filtrate from the barium sulphate. After filtering, the thiosulphate may be detected in the filtrate by the use of iodine and bromine as described above. Table IV. gives some results by this treatment.

TABLE IV.

	$Na_2S_3O_3$ taken. Grm.	$BaSO_4$ precipitated by iodine.	$BaSO_4$ precipitated by bromine.	Remarks.
1.	0·1	None	Abundant	
2.	0·01	None	Good	
3.	0·001	None	Fair	$SnCl_2$ necessary.
4.	0·0005	None	Faint	$SnCl_2$ necessary.
5.	0·0001	None	None	

As will be seen, the test for the thiosulphite by this method of treatment is not so delicate, probably on account of mechanical holding of the barium thiosulphate by the precipitated sulphate and sulphite.

Having determined the limits of accuracy of the method as applied to the sulphite and thiosulphate taken separately, our next experiments were directed toward an investigation of the working of the method when these two acids are found together in solution. Sulphates, almost invariably present with sulphites, are of course quite easily separated by filtration and treating with the barium salt in acid solution. Sulphides if present in the solution would seriously interfere with the working of this method if not removed, being readily oxidised by the iodine or bromine to sulphite, sulphate, or, should sulphur also separate, to thiosulphate. We found in course of our work that in attempting to neutralise a mixture of freshly prepared alkaline sulphide together with a sulphite, we often obtained a precipitate of sulphur. After the removal of the sulphide and sulphate, we were surprised to find on treating with iodine scarcely a trace of sulphite. On treating with bromine, however, an abundant indication of thiosulphate was obtained. It is well known, of course, that thiosulphate may be found by boiling a sulphite with sulphur, but that this reaction should take place so readily and completely seemed to us rather unusual.

For the removal of a sulphide before proceeding with the tests for sulphite and thiosulphate, Grieg Smith recommends the passing of carbon dioxide through the solution until the escaping gas gives no indication of hydrogen sulphide, but Bloxam (CHEM. NEWS, lxxii., 63) calls attention to the tedious and wholly unsatisfactory character of this method of removal, and recommends a mixture of zinc chloride, cadmium chloride, ammonium chloride, and ammonia. We have found that the addition of zinc acetate to a faintly alkaline solution accomplishes the same purpose in an entirely satisfactory manner. The sulphide used in our work was freshly made by passing hydrogen sulphide through a dilute solution of sodium hydroxide. When portions of this solution, still alkaline, were treated with zinc acetate in excess, and the zinc hydroxide and sulphide removed by filtration, the filtrate gave no test for either sulphite or thiosulphate by the application of iodine and bromine as described, and the vapour evolved on boiling caused no darkening of lead paper. The following table shows the results of a few experiments in which tests were made for the sulphite and thiosulphate, after removing a considerable amount of the sulphide in the manner described, and of the sulphate by acidifying and adding barium chloride.

TABLE V.

K_2SO_3 taken. Grm.	$Na_2S_2O_3$ taken. Grm.	$BaSO_4$ precipitated after oxidation with iodine.	$BaSO_4$ precipitated after oxidation with bromine.
0·1	0·01	Abundant	Good.
0·1	0·001	Abundant	Distinct.
0·01	0·1	Good	Abundant.
0·001	0·1	Faint	Abundant.
0·001	0·001	Fair	Fair.

The method as we have modified it may be summarised as follows:—To about 0·1 grm. of the substance to be analysed dissolved in 10 c.m.^{3} of water or more, add sodium, potassium, or ammonium hydroxide to distinct but faintly alkaline reaction. The solution should be neutral or alkaline rather than even faintly acid, owing to the readiness with which sulphur separates. To the alkaline solution add zinc acetate in distinct excess, and filter. The precipitate may be tested for hydrogen sulphide, on acidifying, in the usual manner. To the filtrate add acetic acid, a few drops in excess of the amount necessary to neutralise, and barium chloride, and filter through a double filter. To the filtrate add iodine until the solution takes on a permanent yellow tinge, and then bleach with stannous chloride,—best after adding a few drops of hydrochloric acid to prevent the possible precipitation of a basic salt of tin. A precipitate at this point indicates the sulphite. Filter, add bromine water in faint excess to the filtrate, bleaching again with stannous chloride. A precipitate on adding bromine indicates a thiosulphate originally present.

THE

ACTION OF LIGHT UPON DYED COLOURS.[*]

(Concluded from p. 206).

CLASS III.—MODERATELY FAST COLOURS. (WOOL).

Induline Colours.

Wool Book XIV.

Acid Colours.—

*9. Nigrisine. Sodium salt of an induline-sulphonic acid. S. and J. III. 475.
*10. Brilliant Black EB. Constitution not published.

Basic Colours.—

2*a*. Nigrisine J. Condensation product of *p*-nitroso-dimethyl aniline.
3*a*. Nigrisine. Similar to Nigrisine J. S. and J. III. 502.

Azo Colours.

Acid Colours.—

*5. Naphthol Black 4R. Constitution not published.
8. Jet Black R. From amido-benzene-disulphonic-acid-azo-α-naphthylamine and phenyl-α-naphthylamine. S. and J. III. 150.
11. Naphthylamine Black. From α-naphthylamine disulphonic-acid-azo-α-naphthylamine and α-naphthylamine. S. and J. III. 153.
*41. Acid Black B. Constitution not published.
16. Acid Black 2B. Constitution not published.
*17. Naphthol Black 6B. From α-naphthylamine-disulphonic acid-azo-α-naphthylamine and β-naphthol-disulphonic acid R. S. and J. III. 154.
*18. Naphthol Black 3B. Constitution not published.
*20. Victoria Black B. From sulphanilic acid-azo-α-naphthylamine and β-naphthol-sulphonic acid S. S. and J. III. 149.
*22. Naphthol Black B. From β-naphthylamine-γ-disulphonic acid-azo-α naphthylamine and β-naphthol-disulphonic acid R. S. and J. III. 157.
25. New Victoria Black Blue. Constitution not published.
28. Naphthylamine Black 6B. Constitution not published.
*29. Victoria Black Blue. Constitution not published.
30. Naphthylamine Black 4B. Constitution not published.
31. New Victoria Black B. Constitution not published.
*32. Victoria Black G. Constitution not published.
*33. Victoria Black 5G. Constitution not published.
34. New Victoria Black 5G. Constitution not published.

Wool Book XIV.

Basic Colours.—

*3. Diazine Black. From safranine and phenol.

Direct Cotton Colours.—

3. Benzo Black Blue G. From benzidine-disulphonic acid, with α-naphthylamine-azo-α-naphthol-sulphonic acid NW and α-naphthol-sulphonic acid NW. S. and J. III. 266.
4. Benzo Black Blue R. From tolidine, with α-naphthylamine-azo-α-naphthol-sulphonic acid NW and α-naphthol-sulphonic acid NW. S. and J. III. 266.
5. Benzo Black. Constitution not published.
6. Benzo Black S extra. Constitution not published.
7. Diamond Jet Black OO. Constitution not published.
8. Chicago Grey. Constitution not published.
9. Diamine Jet Black SS. Constitution not published.
15. Diamine Black HW. Constitution not published.
17. Benzo Black Blue 5G. From benzidine-disulphonic acid, with α-naphthylamine-azo-dioxynaphthalene-sulphonic acid S and dioxynaphthalene-sulphonic acid S. S. and J. III. 267.

Direct Cotton Colours Developed.—

6. Diazo Brilliant Black B. From tolidine and α-naphthylamine-sulphonic acid L. Developed with β-naphthol.
7. Diazo Brilliant Black R. Constitution not published. Developed with β-naphthol.

Mordant Colour.—

1. Chrome Black (Cr). Constitution not published.
3. Diamond Black (Cr). From amido-salicylic-acid-azo-α-naphthylamine and α-naphthol-sulphonic acid NW. S. and J. III. 159.
4. Diamond Black NG (Cr). Constitution not published.
5. Diamond Black GA (Cr). Constitution not published.

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[*] Report of Committee, consisting of Dr. T. E. Thorpe (Chairman), Professor J. J. Hummel (Secretary), Dr. W. H. Perkin, Professor W. J. Russell, Captain Abney, Professor W. Stroud, and Professor R. Meldola. (Drawn up by the Secretary). Read before the British Association (Section B); Bristol Meeting, 1898.

Natural Colouring Matters.

Mordant Colours.—

Logwood (Cr) (Fe*). Hæmatoxylon campecianum (wood).

Cochineal (Fe*). Coccus cacti (insect).

Notes.—The colours dyed with the two Nigrisines are medium shades of grey; they do not alter materially in hue during the fading process, and at the end of the third period of exposure they still appear as pale greys. The following colours alter very little in hue while fading, and fade so gradually that they might fairly well be thought worthy of being classed as "Fast Colours":—Nigrisine, Brilliant Black EB, Acid Black B, Naphthol Blacks 3B and 6B, Victoria Blacks B, G, and 5G, Victoria Black Blue. Diazine Black acquires a somewhat yellowish cast at the end of the first period of exposure, and then fades so slowly that even at the end of a year a full grey shade remains.

Several of the artificial black colours in this class are quite as fast to light as the black obtained with logwood on chromium mordant; some indeed seem to be more permanent, and they do not acquire the characteristic olive tint of the faded logwood and chromium black. With iron mordant logwood gives a somewhat faster black than that obtained with chromium; the same appears to be the case with Chrome Black and the various marks of Diamond Black.

Class IV.—Fast Colours. (Wool).

Azo Colours.

Wool Book XIV.

Mordant Colours.—

5. Chrome Black (Fe). Constitution not published.
6. Diamond Black (Fe). From amido-salicylic acid-azo-α-naphthylamine and α-naphthol-sulphonic acid NW. S. and J. III. 159.
7. Diamond Black NG (Fe). Constitution not published.
8. Diamond Black GA (Fe). Constitution not published.

Oxyketone Colours.

Mordant Colours.—

*Alizarin Black SW (Cr) (Fe). Sodium bisulphite compound of dioxy-naphthoquinone. S. and J. III. 385.

*Alizarin Bordeaux G (Fe). Constitution not published.

*Alizarin Bordeaux B (Fe). Tetra-oxy-anthraquinone (1.2.5.8). Quinalizarin. S. and J. III. 403.

Class V.—Very Fast Colours. (Wool).

Oxyketone Colours.

Wool Book XIV.

Mordant Colours.—

Alizarin Bordeaux GG (Fe). Constitution not published.

Silk Patterns.

Most of the foregoing colours were also dyed on silk, and the patterns were exposed to light along with the woollen patterns. The relative fastness of the various colours is generally the same as on wool, and a special classification for silk seems unnecessary.

DISTRIBUTION AND QUANTITATIVE OCCURRENCE OF VANADIUM AND MOLYBDENUM IN ROCKS OF THE UNITED STATES.[*]

By W. F. HILLEBRAND.

Aside from its well known mineral combinations, vanadium has long been known to occur in magnetites and other iron ores. Hayes in 1875 reported its occurrence in a great variety of rocks and ores. Quoting from "Thorpe's Dictionary of Chemistry," "it is said to be diffused with titanium through all primitive granite rocks (Dieulafait) and has been found by Deville in bauxite, rutile, and many other minerals, and by Bechi and others in the ashes of plants and in argillaceous limestones, schists, and sands . . . ." It is further reported to comprise as V_2O_5 0·02 to 0·07 per cent of many French clays, 0·02 to 0·03 per cent of some basalts, 0·24 per cent of a coal of unknown origin and 0·45 per cent of one from Peru, amounting to 38·5 per cent ond 38 per cent of the ash and noted respectively by Mourlot and Torrico y Meca. Doubtless many other instances of its occurrence have been noted.

In Table I. is shown its quantitative occurrence and distribution in a large number and variety of igneous rocks of the United States, arranged according to their silica contents; and in Table II. the same data are given for a few of the component minerals separated from some of those rocks, while Table III. shows its presence in metamorphosed and secondary rocks by a few examples of roofing slates and schists, and especially by two composite samples representing 253 sandstones and 498 building limestones. These last two afford positive proof of its general distribution through rocks of those classes. Incidentally some information has been acquired as to molybdenum. Owing to lack of entire certainty as to its condition of oxidation, the vanadium is tabulated in terms of both V_2O_5 and V_2O_3, a point which will be reverted to later on. With very few exceptions, the amount of each sample taken for analysis was 5 grms. The reagents used were carefully tested and found free from vanadium and molybdenum. Except Nos. 38, 39, 47, 52, and 53, by Dr. H. N. Stokes, all determinations are by myself.

Of the igneous rocks specimens were so selected as to represent not only many widely separated localities, but also numerous varieties from the least siliceous up to those high in silica, in order to ascertain whether a preconceived opinion that the vanadium accompanied chiefly the less siliceous rocks was well founded or not. The choice was, however, confined largely to those rocks analysed in this laboratory within the past three or four years of which a supply of powder remained after the original analyses had been completed, and hence the list is perhaps not fully representative. Nevertheless it permits of drawing certain conclusions, the chief of which is that the vanadium predominates in the less siliceous igneous rocks and is absent—or nearly so—in those high in silica. The inference, based on the existence of the mineral roscoelite, classed as a vanadium-mica, at once suggests itself, that the ultimate source of the vanadium may be one or more of the heavier silicates—such as the biotites, pyroxenes, and amphiboles, and a few tests on all the available mineral separation products lend strong support to this view. For instance, the amphibole gabbros 7 and 11 show 0·038 per cent and 0·02 per cent V_2O_3, while the anphiboles 7*a* and 11*a* separated from them give 0·062 per cent and 0·037 per cent; the pyroxenic gneiss 23 shows 0·083 per cent against 0·127 from its contained biotite 23*a*; the diorite 29 with 0·031 per cent contains an amphibole 29*a* with 0·066 per cent; from 0·011 per cent in the quartz-mica diorite 45 and 0·012 per cent in the quartz monzonite 46 the percentages rise to 0·048 and 0·066 in their separated biotites 45*a* and 46*a*. The pyroxene 21*a* shows, however, practically the same amount as its mother rock, the syenitic lamprophyre 21.

In most of these cases, notably the last one, the vanadium in the separated mineral is not sufficiently in excess of that in the rock from which it was taken to account for all of that found in the latter. Hence, if the determinations are correct, it must also be a constituent of some other mineral than the one analysed. In roscoelite the trivalent condition of vanadium corresponding to the oxide V_2O_3 is now recognised as probable, although Roscoe's analysis reports V_2O_5, and Genth's an oxide intermediate

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[*] Read before the Geological Society of Washington, D.C., May 25, 1898. From the *American Journal of Science*, vol. vi., p. 209,

TABLE I.—*Igneous Rocks.*

No.	Name and locality of occurrence.	SiO_2. Per cent.	V_2O_5 = Per cent.	V_2O_3. Per cent.	Mo. Per cent.
1.	Melilite-nepheline basalt, Uvalde Co., Texas	38	0·054	0·045	
2.	Nephelinite, Uvalde Co., Texas	40	0·042	0·035	
3.	Saxonite, Douglas Co., Oregon	41·5	None	None	
4.	Diorite, Cecil Co., Maryland	44	0·062	0·052	
5.	Gabbro, Adirondack region, New York	45	0·02	0·017	
6.	Plagioclase basalt, Uvalde Co., Texas	45	0·048	0·04	
7.	Amphibole gabbro, Alpine Co., California	46	0·046	0·038	None
8.	Plagioclase gneiss, Amador Co., California	46·5	0·033	0·027	
9.	Diorite, Mitchell Co., North Carolina	47	0·05	0·042	
10.	Porphyry, La Plata Co., Colorado	47	0·06*	0·05*	
11.	Amphibole gabbro, Tuolumne Co., California	47	0·024	0·02	None
12.	Orthoclase-bearing basalt, Uvalde Co., Texas	48 ?	0·048	0·04	
13.	Orthoclase-bearing basalt, Uvalde Co., Texas	48	0·02	0·017	
14.	Norite, Cecil Co., Maryland	48	0·023	0·019	
15.	Gabbro, Union Co., Tennessee	48	0·038	0·032	
16.	Gabbro, Douglas Island, Alaska	48	0·055	0·046	None
17.	Nepheline basanite, Colfax Co., North Mexico	48·5	0·044	0·037	
18.	Olivine basalt, Kruzoff Island, Alaska	49·5	0·054	0·045	None
19.	Diabase, Mt. Ascutney, Vermont	49·5	0·034	0·028	
20.	Phonolite, Cripple Creek, Colorado	50	0·033	0·027	
21.	Syenite lamprophyre, Prowers Co., Colorado	50·5	0·04	0·033	
22.	Augite-andesite porphyry, Electric Peak, Wyoming	50·5	0·045	0·038	
23.	Pyroxenic gneiss, Calaveras Co., California	51·5	0·10	0·083	None
24.	Labradorite porphyrite, Michigamme iron district, Michigan	52·5	0·048	0·04	
25.	Pyroxenite, Cecil Co., Maryland	53	0·04	0·034	None
26.	Orendite, Sweetwater Co., Wyoming	54	0·022	0·018	
27.	Andesite, El Paso Co., Colorado	54 ?	0·018	0·015	Trace ?
28.	Nepheline syenite, El Paso Co., Colorado	54·5	0·022	0·018	Trace ?
29.	Diorite, Butte and Plumas Cos., California	54·5	0·037	0·031	None
30.	Quartz diorite, Cecil Co., Maryland	55	0·043	0·036	None
31.	Diorite, La Plata Co., Colorado	55·5	0·038	0·032	
32.	Camptonite ? San Miguel Co., Colorado	55·5	{ Lost, but considerable.		
33.	Phonolite, Colfax Co., North Mexico	56	Trace	Trace	
34.	Augite-bronzite andesite, Unga Island, Alaska	56·5	0·046	0·038	None
35.	Andesite, El Paso Co., Colorado	57 ?	0·025	0·021	Trace ?
36.	Spilosite, Michigamme iron district, Michigan	58	0·03	0·025	None
37.	Hornblende granite, Cecil Co., Maryland	58·5	0·022	0·018	None
38.	Latite, Tintic district, Utah	60	0·007	0·006	None
39.	Monzonite, Tintic district, Utah	60	0·024	0·02	Trace
40.	Diorite porphyry, La Plata Mts., Colorado	60·5	0·02	0·017	
41.	Trachyte-andesite tuff, Tuolumne Co., California	62·5	0·017	0·014	
42.	Diorite, Douglas Island, Alaska	63	0·012*	0·01*	None
43.	Rhyolite, San Miguel Co., Colorado	64·5	0·004	0·003	Trace
44.	Syenite, Mt. Ascutney, Vermont	65·5	Trace ?	Trace ?	
45.	Quartz-mica diorite, Tuolumne Co., California	65·5	0·013	0·011	Trace
46.	Quartz monzonite, Calaveras Co., California	67	0·014	0·012	None
47.	Rhyolite, Tintic district, Utah	69	0·009	0·008	Trace
48.	Quartz diorite, Amador Co., California	69·5	0·005	0·004	Trace
49.	Trachyte, Highland Co., Virginia	69·5	Trace ?	Trace ?	
50.	Biotite granite, Amador Co., California	70·5	Trace	Trace	Trace
51.	Rhyolite, Crater Lake, Oregon	71	0·004	0·003	Faint trace
52.	Monzonite (altered), Tintic district, Utah	71	0·021	0·017	None
53.	Rhyolite quartz-porphyry, Tintic district, Utah	71·5	0·016	0·013	None
54.	Rock between rhyolite and dacite, Sutter Co., California	71·5	Trace	Trace	
55.	Syenite porphyry, Mt. Ascutney, Vermont	73	None	None	
56.	Granite porphyry, Mt. Ascutney, Vermont	73·5	None	None	
57.	Granite, Union Co., Tennessee	76·5	None	None	

* Approximate.

TABLE II.—*Component Minerals from certain of the above Igneous Rocks.*

No.	Name and source.	SiO_2. Per cent.	V_2O_5 = Per cent.	V_2O_3. Per cent.	Mo. Per cent.
7*a*.	Amphibole from 7	?	0·075	0·062	None
11*a*.	Amphibole from 11	46	0·044	0·037	None
21*a*.	Pyroxene from 21	51·5	0·043	0·036	
23*a*.	Biotite from 23	36·5	0·153	0·127	None
29*a*.	Amphibole from 29	50	0·08	0·066	
45*a*.	Biotite from 45	?	0·057	0·048	None
46*a*.	Biotite from 46	35·5	0·08	0·066	

TABLE III.—*Miscellaneous.*

No.	Name and locality of occurrence.	SiO_2. Per cent.	V_2O_5 = Per cent.	V_2O_3. Per cent.	Mo. Per cent.
58.	Epidotic schist, Mitchell Co., North Carolina	48	0·057	0·047	
59.	Quartz schist, Madera Co., California	79	Trace	Trace	
60.	Serpentine, Connecticut Valley, Massachusetts	38·5	None	None	
61.	Sea green roofing-slate, West Pawlet, Vermont	68	0·017	0·014	
62.	Two red roofing-slates (equal parts), Washington Co., New York	67 56	0·008	0·007	
63.	253 sandstones	78·5	0·003	0·003	
64.	498 building limestones	14	0·004	0·004	

between V_2O_3 and V_2O_5. This assumption seems to be necessary if the mineral is to be regarded as a mica, and it is then doubtless the equivalent of trivalent iron or aluminum. It would then be natural to look for it in the aluminous or ferric silicates of igneous rocks, certain biotites, pyroxenes, and hornblendes, and its absence in such minerals as serpentine and chrysolite, as shown by analyses 3 and 60, appears natural enough.

Few and inconclusive as the above comparisons are, they seem to favour strongly this view as to the source of the vanadium, and in a measure are confirmatory of the observation of Hayes (*Proc. Am. Ac.*, 1875, x., 294), who, rather indefinitely, associates it with phosphorus and proto-salts of iron and manganese, which are usually more prominent components of basic than of acid rocks.

We are probably justified by the evidence in tabulating the vanadium as V_2O_3 in analyses of igneous and some metamorphic rocks which have undergone little or no oxidation; but with sandstones, clays, limestones, &c., which are of more or less decided secondary origin, this is probably not the case. The probabilities are there largely in favour of its acid character and the existence of various vanadates of calcium, iron, aluminum &c., in which case it should appear in analytical tables as V_2O_5 (see Note).

It was not until the greater part of the above tests had been finished that any careful attempt was made to identify molybdenum as well as vanadium. From the evidence gathered during the latter part of the work it would seem that molybdenum when it does occur is a much less important constituent quantitatively than vanadium, and that, unlike the latter, it accompanies the more acid rocks. Molybdenite is a well-known accessory constituent of some granites, &c., but in the above instances its amount was extremely small, and no hint was obtained as to its state of combination.

NOTE.—In the regular course of analysis vanadium will be weighed with alumina, iron, titanium, &c., since it is precipitated by both ammonia and sodium acetate in presence of those and other metals; hence the alumina percentages in nearly all rock analyses heretofore made are subject to correction for the vanadium the rock may have held. This correction is of course to be made in terms of V_2O_5, and not of V_2O_3.

All determinations of iron are likewise affected by its presence whether as V_2O_5 or V_2O_3. As V_2O_3 it will make the FeO appear too high in the proportion $V_2O_3 : 4FeO$, or 150·8 : 288, an error which becomes appreciable in some of the basic rocks, and amounts to 0·25 per cent in the biotite 23*a*. As V_2O_5 the FeO will not be affected, but in either condition the Fe_2O_3 will need correction and to a different extent, according as the titration of iron is made after reduction by hydrogen sulphide or by hydrogen. If the former is used, as should always be the case in presence of titanium, the vanadium is reduced by it to V_2O_4, which in its action on permanganate is equivalent to two molecules of FeO representing one of Fe_2O_3, or only one-half as great as the influence on the FeO titration of the same vanadium as V_2O_3. An example will make this clear:—

Found 2·50 per cent apparent FeO in a rock containing 0·13 per cent V_2O_3.
Deduct 0·25 per cent FeO equivalent in its action on $KMnO_4$ to 0·13 V_2O_3,
Leaving 2·25 per cent FeO corrected.
Found 5·00 per cent apparent total iron as Fe_2O_3 in the same rock.
Deduct 0·14 per cent Fe_2O_3 corresponding to 0·13 per cent V_2O_3,
Leaving 4·86 per cent corrected total iron as Fe_2O_3.
Deduct 2·50 per cent Fe_2O_3 equivalent to 2·25 per cent FeO,
Leaving 2·36 per cent Fe_2O_3 in the rock.

Failure to correct for the vanadium in both cases would have made the figures for FeO and Fe_2O_3 respectively 2·50 and 2·22, instead of 2·25 and 2·36 as shown above.

Chemical Method employed.

In conclusion, it is proper to outline the method by which the foregoing tests were carried out, and to indicate the precautions that must be observed in order to insure good results.

Quite a number of workers have busied themselves with the problem of vanadium estimation in ores and rocks, particularly magnetites and other iron ores, and the methods used have been often diverse in parts, if not altogether. There is nothing absolutely novel in the following, except that chromium and vanadium when together need not be separated, but are determined, the former colorimetrically, the latter volumetrically, in the same solution as detailed elsewhere (*Jour. Am. Chem. Soc.*, xx., pp. 454 and 461, 1898).

Five grms. of the rock are thoroughly fused over the blast, with 20 grms. of sodium carbonate and 3 of sodium nitrate. After extracting with water and reducing manganese with alcohol it is probably quite unnecessary, if the fusion has been thorough, to re-melt the residue as above, though for magnetites and other ores containing larger amounts of vanadium than any of these rocks, this may be necessary, as Edo Claassen has shown (*Am. Chem. Jour.*, viii., 437). The aqueous extract is next nearly neutralised by nitric acid, the amount to be used having been conveniently ascertained by a blank test with exactly 20 grms. of sodium carbonate, &c., and the solution is evaporated to approximate dryness. Care should be taken to avoid over-running neutrality, because of the reducing action of the nitrous acid set free from the nitrite; but when chromium is present it has been my experience that some of this will invariably be retained by the precipitated silica and alumina, though only in one case have I observed a retention of vanadium, it being then large. The use of ammonium nitrate instead of nitric acid for converting the sodium carbonate into nitrate did not seem to lessen the amount of chromium retained by the silica and alumina.

As a precautionary measure, therefore, and always when chromium was to be estimated also, the silica and alumina precipitate was evaporated with hydrofluoric and sulphuric acids, the residue fused with a little sodium carbonate, and the aqueous extract again nearly neutralised with nitric acid and boiled for a few moments, the filtrate being added to the main one.

Mercurous nitrate was now added to the alkaline solution in some quantity so as to obtain a precipitate of considerable bulk, containing chromium, vanadium, molybdenum, tungsten, phosphorus, and arsenic, should all happen to be in the rock, and also an excess of mercurous carbonate to take up any acidity resulting from the decomposition of the mercurous nitrate. Precipitating in a slightly alkaline instead of a neutral solution renders the addition of precipitated mercuric oxide unnecessary for correcting this acidity. If the alkalinity, as shown by the formation of an unduly large precipitate, should have been too great, it may be reduced by careful addition of nitric acid until an added drop of mercurous nitrate no longer produces a cloud.

After heating and filtering, the precipitate is ignited in a platinum crucible after drying and removing from the paper to obviate any chance of loss of molybdenum and of injury to the crucible by reduction of phosphorus or arsenic. The residue is fused with a very little sodium carbonate, leached with water, and the solution if coloured yellow filtered into a graduated flask of 25 or more c.c. capacity. The chromium is then estimated accurately in a few minutes by comparing with a standard alkaline solution of potassium monochromate (*Journ. Am. Chem. Soc.*, 1898, xx., 454). Then, or earlier in absence of chromium, sulphuric acid is added in slight excess, and molybdenum and arsenic together, with occasional traces of platinum, are precipitated by hydrogen sulphide, preferably in a small pressure bottle.* If the colour of the precipitate indicates absence of arsenic, the filter with its contents is carefully ignited in porcelain, and the delicate sulphuric acid test for molybdenum is applied.

The filtrate, in bulk from 25 to 100 c.c. is boiled in a current of carbon dioxide to expel hydrogen sulphide, and titrated at a temperature of 70—80° C., with a very dilute solution of permanganate representing about 1 m.grm. of V_2O_5 per c.c. as calculated from the iron strength of the permanganate, 1 molecule of V_2O_5 being indicated for each one of Fe_2O_3. One or two checks are always to be made by reducing again in a current of sulphur dioxide gas, boiling this out in a current of carbon dioxide again, and repeating the titration.

As shown in a previous paper (*Journ. Am. Chem. Soc.*, 1898, xx., 464) the presence of even thirty times as much Cr_2O_3 as V_2O_5 does not prevent a satisfactory determination of the vanadium if the precautions therein given are observed, provided there is present not less than ½—1 m.grm. of V_2O_5 in absolute amount. In absence of chromium less than half a m.grm. can be readily estimated. The phosphoric acid almost invariably present does not affect the result.

In case the volume of permanganate used is so small as to make doubtful the presence of vanadium, it is necessary to apply a qualitative test, which is best made as follows:—The solution is evaporated and heated to expel excess of sulphuric acid, the residue is taken up with 2 or 3 c.c. of water and a drop or two of dilute nitric acid, and a couple of drops of hydrogen peroxide are added. A characteristic brownish tint indicates vanadium. Unless the greater part of the free sulphuric acid has been removed the appearance of this colour is sometimes not immediate and pronounced; hence the above precaution.

The above is a surer test to apply than the following:—Reduce the bulk to about 10 c.c., add ammonia in excess, and introduce hydrogen sulphide to saturation. The beautiful cherry-red colour of vanadium in ammonium sulphide solution is much more intense than that caused by hydrogen peroxide in acid solution, but the action of ammonia is to precipitate part or all of the vanadium with the chromium or aluminum that may be present or with the manganese used in titrating, and ammonium sulphide is unable to extract the vanadium wholly from these combinations. Usually, however, the solution will show some colouration, and addition of an acid precipitates brown vanadium sulphide, which can be collected, ignited, and further tested if desired.

Summary of Results.

Vanadium occurs in quite appreciable amounts in the more basic igneous and metamorphic rocks, up to 0·08 per cent or more of V_2O_3, but seems to be absent—or nearly so—from the highly siliceous ones. The limited evidence thus far obtained points to the heavy ferric aluminous silicates as its source—the biotites, pyroxenes, amphiboles. As opportunities offer, further evidence will be accumulated, and it is hoped that other chemists will lend their aid.

Limestones and sandstones appear to contain very small amounts of vanadium, as shown by analysis of a composite sample of each aggregating over 700 different occurrences.

From the few tests for molybdenum it appears as if this element were confined to the more siliceous rocks. It is present in no observed case in amount sufficient for quantitative measurement when operating on 5 grms. of material.

Note.—Since the above was written, a few tests have been made on minerals of which powdered samples were at hand. A phlogopite from Burgess, Canada, gave 0·007 per cent V_2O_3. Mica from Laurel Hill, Georgia, gave 0·026 per cent V_2O_3. Protovermiculite from Magnet Cove, Ark., gave 0·04 per cent V_2O_3. Hallite from Chester Co., Pa., gave 0·01 per cent V_2O_3. Jeffersonite, from Franklin, N.J., gave none, and a non-ferruginous amphibole from St. Lawrence Co., N.Y., gave a faint trace.

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* From a sulphuric solution the separation of molybdenum by hydrogen sulphate is much more rapid and satisfactory than from a hydrochloric solution.

NOTICES OF BOOKS.

Elements of General Chemistry, with Experiments. By John H. Long. Chicago: E. H. Colegrove, Sales Agent. 1898. Pp. vi.—408. 8vo. Illustrated.

In preparing this book the author, who is Professor of Chemistry in the North-western University, has used a part of his work "Experimental and Analytical Chemistry," long since out of print, and he has added enough new matter to make of it a complete text-book of elementary general chemistry, sufficient for college students beginning the subject. In the Preface Dr. Long remarks that in too many instances the student is introduced to qualitative analysis as his first laboratory work, and this is followed by gravimetric analysis to complete a course: this plan gives the beginner a distorted idea of the relative importance of analytical chemistry in the study of the science, whereas a knowledge of the properties of a substance, the methods of its preparation, and its uses, is far more important for the beginner than acquaintance with methods of separation. On these grounds the author has introduced illustrative experiments (to the number of 174) throughout the work, and the student is advised that he should consider each experiment performed as a question, and the results obtained as the answers.

In the Introduction the student is made acquainted with the three states of matter, solution, crystallisation, precipitation, and the characteristics of physical and chemical changes, by the assistance of thirty-seven simple experiments and explanatory text; then follows the consideration of oxygen and hydrogen and their compounds; after these the elements are treated in a logical order in twenty-three chapters, concluding with the platinum group.

The illustrative experiments are well selected, and the directions for conducting them are clear, though in some cases a simple woodcut would help the student's comprehension.

A blemish in the make-up of the book, in no wise affecting its accuracy, is the fact that the running headlines remain unchanged throughout the 400 pages, whereas the odd-numbered pages ought to indicate to which chapter they belong. The work seems to be free from typographical errors, and there is an index. H.C.B.

CORRESPONDENCE.

FIXATION OF NITROGEN.

To the Editor of the Chemical News.

Sir,—Provisional Protection has recently been obtained for the manufacture of ammonia by the destructive distillation of hydrocarbons in the presence of nitrogen, relying on the nature of nascent hydrogen to combine with nitrogen.

This is simply adopting the natural process by which ammonia is formed in gas-works with the nitrogen of the coal.

The whole question of the employment of nascent hydrogen is a large one, and it is in this direction that success must be looked for.—I am, &c.,

B. Piffard.

MEETINGS FOR THE WEEK.

Thursday, Nov. 3rd.—Chemical, 8. "A Determination of the Equivalent of Cyanogen," by George Dean, B A. "Action of Light on Platinum, Gold, and Silver Chlorides," by E. Sonstadt. "Methanetrisulphonic Acid," by E. H. Bagnall, B.Sc. "A Composite Sodium Chlorate Crystal in which the Twin Law is not followed," by W. J. Pope. "Composition of American Petroleum," by Sydney Young, D.Sc., F.R.S. "Separation of Normal and Iso-heptane from American Petroleum," and "Action of Fuming Nitric Acid on the Paraffins and other Hydrocarbons," by F. E. Francis, B.Sc., and Sydney Young, F.R.S. "Boiling-points and Specific Gravities of Mixtures of Benzene and Normal Hexane," by D. H. Jackson, M.A., and Sydney Young, F.R.S.

THE CHEMICAL NEWS.

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ON THE SUPPOSED NEW GAS, ETHERION.

By Sir WILLIAM CROOKES, F.R.S.

In the Chemical News for the 21st of October last appeared an article giving an account of "Etherion: a New Gas," by Mr. Charles F. Brush. This was only an abstract of the complete paper read by Mr. Brush before the American Association for the Advancement of Science, at Boston, on August 23, and it would not be right to enter into detailed criticism of the results claimed by the author until his complete paper is available. I may, however, be permitted to bring forward some old researches, published and unpublished, which tend, in my opinion, to show that the new gas, Etherion, may be nothing more than aqueous vapour.

Dating from my early work on "Repulsion resulting from Radiation," I noticed in 1873* that a little aqueous vapour thrown into the vacuum converted into attraction the repulsion due to radiation. I worked on this subject for some years, and in 1876† I was experimenting on the effect of radiation exerted by the flame of a candle on discs of pith at the ends of a light torsion beam suspended in a vacuum by means of a delicate silk fibre. The disc at one end of the beam was coated with lamp-black, and the disc at the other end was left in its natural state. The observations bearing on the action of aqueous vapour are quoted from the paper itself:—

"During the exhaustion of one of these pieces of apparatus, an action of aqueous vapour was observed which explained some of the anomalies I had met with in the course of this investigation. The apparatus had a little water in it; and although the mercury pump brought the gauge to within about 8 m.m. of the barometric height in the course of ten minutes, the tension of the aqueous vapour prevented it from rising higher. After working the pump for several hours, and gently warming the different parts of the apparatus, the liquid water was evaporated, and only aqueous vapour remained. The gauge now rapidly rose to the height of the barometer, the apparatus necessarily being filled with the residual aqueous vapour. On bringing a lighted candle near the discs, I expected to see the black one violently repelled; but instead of that the connecting arm set equatorially, showing that the radiation from the candle within a few inches of the discs repelled the white one as strongly as it did the black. The pump was kept in action, and oil of vitriol was passed through it once or twice. This was continued for about four hours, and on testing the apparatus from time to time with a candle the repulsion of the black disc gradually increased, the arm setting at a greater and greater angle from the equatorial position, but at no time getting very strongly deflected. An accident happening to one of the tubes of the pump, it was necessary to let air into the apparatus; it was passed in slowly over oil of vitriol. As soon as the pump was mended, exhaustion of the apparatus was re-commenced. As soon as the gauge rose within 6 m.m. of the barometric height, the candle was seen to repel the black disc. At 3 m.m. the superior repulsion of the black over the white disc was sufficient to cause the arm to set 45°; and as the exhaustion got better, the repulsion of the black disc increased, until—at the point where the gauge and barometer were level—the candle exerted a strong action many feet off, and when brought close to the instrument set the bar and discs in most violent agitation—the black disc being driven violently away, and the connecting arm swinging rapidly on each side of the axial position. This experiment shows that the presence of even a small quantity of aqueous vapour in the exhausted apparatus almost—if not quite—neutralises the more energetic action which luminous rays appear to exert on a blackened surface. In the first case, even when the gauge and the barometer were appreciably level, and the pump had been working for some hours, the superior repulsion of the black over the white was not so strong as it was in the second case when the gauge was several m.m. below the barometer."

Soon after the above experiments were tried, the radiometer was discovered, and in June, 1886, I wrote,* that if residues of gases other than air were in the radiometer the phenomena of repulsion were different in degree, although similar in kind. Thus aqueous vapour was found to retard the force of repulsion to a great extent, and carbonic acid acted in a similar though less degree.

In 1881 I entered more fully into the retarding effect of water vapour on the repulsion due to radiation on bodies free to move in different gases at high vacua, and, in a paper on "The Viscosity of Gases at High Exhaustions," I wrote†:—

"The presence of water vapour (in air) shows itself in the very slight amount of repulsion produced by radiation. Repulsion commences in air at a pressure of 12 m.m., whilst at a higher exhaustion the maximum effect rises to over forty divisions. Here, however, repulsion, does not begin till the exhaustion is higher than the barometer gauge will indicate, whilst the maximum action after long-continued pumping is only nine divisions. This confirms the results frequently met with in my researches on "Repulsion resulting from Radiation," where the presence of even a trace of aqueous vapour was found to have a strong action in diminishing the sensitiveness of the radiometer and other instruments."

"I was unable to take pressures after 1·0 m.m. as the McLeod measuring apparatus does not give trustworthy indications when aqueous vapour is present. As soon as the pressure in the measuring tube rises above the tension of aqueous vapour, water condenses in it, and measurements can no longer be taken."

I give these extracts to show that the anomalous action of aqueous vapour had been obtruding itself on my notice since 1878. With the object of ascertaining more definitely what this action was, in 1880 I commenced some experiments on heat conduction in air and other highly rarefied gases. Of this research only the first part was published, namely that referring to the conduction of heat across a space containing highly rarefied dry air. The experiments in hydrogen, aqueous vapour, and other gases are still unpublished. It is from the results obtained with these gases that I am led to believe that etherion will turn out to be water vapour. In coming to this conclusion I can obviously only argue on the few pieces of evidence given by Mr. Brush in the abstract before me;‡ when the complete paper comes to hand it may contain other evidence, for it is unlikely that the author would announce so important a discovery on the doubtful evidence at present given.

The properties of etherion, given in the abstract, are as follows:—It is presumably elementary, and is a constituent of the atmosphere. It has enormous heat-conductivity at very low pressures, ranging from nearly as good as hydrogen at a pressure of 36 millionths of an atmosphere, to twenty-seven times as good as hydrogen at 0·38 of a millionth. It is absorbed from the atmosphere by glass and is evolved by heating the glass in vacuo, being reabsorbed on cooling. It is also absorbed by phosphorus

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* *Phil. Tranz.*, vol. clxiv., Part 2, pp. 515-517.

† *Phil. Trans.*, vol. clxvi., Part 2, p. 329.

* *Proc. R. S.*, vol. xxv., No. 172, p. 140.

† *Phil. Trans.*, vol. clxxii., Part 2, p. 428.

‡ Chemical News, vol. lxxviii., p. 197, Oct. 21, 1898.

pentoxide and by soda-lime; on this account no desiccating agent could be used.

For the following reasons I consider etherion to be water vapour:—

Firstly, as to its absorption by glass and the evolution of the gas on heating the glass in a vacuum. I must begin with a quotation from a paper I wrote in 1879, "Contributions to Molecular Physics in High Vacua."*

> "I have already mentioned that platinum will fuse in the focus of converging molecular rays projected from a concave pole. Another piece of apparatus was constructed in which a plate of German glass was held in the focus of the molecular bombardment. The vacuum was so good that no hydrogen or other lines could be seen in the spectrum of the emitted light. The focus was now allowed to play on the glass, when the glass soon became red-hot. Gas appeared in the tube, and hydrogen lines now were visible in the spectrum. The gas was pumped out until hydrogen disappeared from the spectrum. It was now possible to heat the glass to dull redness without hydrogen coming in the tube; but as soon as the heat approached the fusing-point, the characteristic lines appeared. It was found that however highly I heated the glass, and then pumped the tube free from hydrogen, I had only to heat the glass to a still higher temperature to get a hydrogen spectrum in the tube. I consider the hydrogen spectrum comes from vapour of water, which is obstinately held in the superficial pores, and which is not entirely driven off by anything short of actual fusion of the glass. The bubbles noticed when the disintegrated and fused surface of the tube was examined under the microscope are probably caused by escaping vapour of water. A piece of glass from a tube which had cracked at incipient fusion was examined under the microscope. The surface appeared curiously crumpled up and filled with minute bubbles, as if the glass had been boiling."

I have repeated the above-described experiment in a slightly modified form, using as a source of vapour or gas powdered glass which had been for some time exposed to the air.

A vacuum tube was made with a narrow tube connecting the end bulbs carrying the poles, in such a way that the spectrum could be examined "end on." At one part a supplementary tube was attached, containing about 10 grms. of powdered soda-glass. The phosphoric drying tube had been removed from the pump, and the apparatus was exhausted. The powdered glass was then gently heated in a vessel of hot water, when the gauge sank to about 9 m.m. and remained there for some time. The spectrum of the gas showed water vapour very strongly, a trace of nitrogen, and a little carbonic acid. Exhaustion was continued until the gauge rose to ¼ m.m., when the glass powder was again heated a little more than at first. The gauge again sank to 9 m.m., and the spectrum showed the same gaseous mixture as before. Again heat was applied to the powdered glass, the gauge was depressed, and the pump set going. This was repeated several times, the last few spectroscopic testings showing nothing but water and carbonic acid. Finally, after thorough exhaustion, the powdered glass was heated strongly until the tube and powder melted together, and the gauge sank about 4 m.m. The spectroscope again showed water and carbonic acid, and continued so to do until all the gas had been pumped out.

This experiment, corroborating the one of 1879, proves that air-dry glass condenses on its surface a considerable quantity of water and carbonic acid which does not come off in a vacuum until heat is applied. After a sufficient amount of water vapour to show itself spectroscopically has been driven off, and a non-conducting vacuum again formed, a further increase of temperature will drive off a fresh quantity of water, and the alternations of exhausting and driving off water can be performed many times, the temperature being each time raised higher and higher until the bulb collapses. No line was seen in any of the spectra which could be ascribed to an unknown gas; none but those of water and carbonic acid being observed.

Secondly, as to the conductivity for heat of gases and vapours other than air, I will first give briefly some results of my unpublished work on this subject.

Dry hydrogen at atmospheric pressure is a much better conductor for heat than is air, but this superiority falls off as the pressure diminished, and at a high exhaustion air and hydrogen are about equal. Carbonic acid is a worse conductor than air at all pressures.

Starting with water in the thermometer apparatus, and then pumping until only a just visible trace of liquid water was left, and the gauge was steady at 9 m.m., the conductivity for heat was close upon that of air at the ordinary pressure. Continuing exhausting until all visible water had disappeared, and the gauge commenced to rise above 9 m.m., the conductivity diminished, and at the higher exhaustions, when the gauge and barometer are apparently on a level, the conductivity of the residual vapour was still less, although not so great as that of air or hydrogen. At the highest exhaustion I could get after the pump had been going for some hours,[*] the thermometer in the bulb required 295 seconds to rise 25°. At similar high vacua with air the time required to rise 25° was 491 seconds, and with a hydrogen vacuum the time required was 441 seconds.

These experiments, of which only the results are here given, show that at high vacua water-gas is a better conductor than either air or hydrogen at similar pressures.

But Mr. Brush gives as the most remarkable property of etherion its heat conductivity, which is 27 times that of hydrogen at a pressure of 0·38 of a millionth of an atmosphere. Now it has been found that as water-gas is rarefied its heat conductivity diminishes in a greater ratio than that of hydrogen. At the time I tried these experiments I could not conveniently obtain or measure pressures below 1 millionth, but at these high vacua water-gas gains so rapidly on hydrogen, that I am prepared to believe that at Mr. Brush's low pressure of 0·38 millionth the ratio may even be as great as that he ascribes to etherion.

Within the last few days I have repeated the experiment with the thermometer in the bulb with which the foregoing experiments were tried, but using powdered soda glass as a source of gas. The phosphoric acid drying tubes were removed. and the apparatus was well exhausted. The glass was at first gently heated and the evolved gas pumped out. This was repeated several times, until at last, after very strongly heating the tube of glass powder until it melted, it was sealed off, and observations were taken of the heat conductivity of the residual gas. The time occupied in the thermometer sinking 25° C. at the various degrees of high exhaustion were very near those for water vapour, and the conductivity fell off as pressure diminished more closely according to the water curve than the hydrogen curve. The falling off was not, however, quite so great as when pure water was used. This I ascribe to the presence of carbonic acid, which is always evolved, with water, when glass is strongly heated in a vacuum.

As I have already said, I have no wish to speak at all positively on a paper of which only an abstract, probably an imperfect one, is to hand. But on the evidence at present available I consider it more probable that etherion is water vapour than that it is a new elementary gas, and this is corroborated by the observations made by Mr. Brush, that etherion is absorbed by phosphoric acid and soda-lime, as well as by the powdered glass from which it has previously been driven off by heat.

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[*] *Phil. Trans.*, vol. clxx., Part 2, pp. 658, 659.

[*] I cannot use the McLeod gauge with aqueous vapour, owing to its condensing in the pressure tube.

AN EXAMINATION OF THE PRODUCTS OBTAINED BY THE DRY DISTILLATION OF BRAN WITH LIME.

By W. F LAYCOCK, Ph.D.

(Concluded from p. 212).

Examination of B.

THE black oil weighed 420 grms. On twice distilling, 220 grms. of oil* boiling between 70—325° passed over, and about 200 grms. of tar remained in the still. The distillate was shaken with 200 c.c. of 5 per cent hydrochloric acid. The acid solution, which was of a dark red colour, was separated from the oil, and the latter washed with small quantities of water until free from acid. The acid extract and the washings were subsequently mixed and filtered from a little resinous matter. On treating the filtered solution with excess of sodium hydrate, a black oil separated out, and was extracted with ether. The aqueous residue was distilled with steam. No aldehyds were detected in the distillate on testing with ammoniacal silver nitrate and decolorised magenta solutions.

The ethereal extract was evaporated, and the remaining oil distilled. About 23 grms. of a yellow oil, boiling from 70—290° and containing 13 per cent of nitrogen, was obtained. It was boiled with excess of hydrochloric acid for some hours, and, after filtering from a little pyrrol-red, the saline solution was evaporated to dryness on the water-bath. The dark crystalline mass which remained was distilled with excess of solid caustic potash in an oil bath. The distillate was dissolved in ether, dried with solid caustic potash, and, after evaporation of the ether, distilled. About 10 grms. of oil passed over; it boiled from 80—270°, and was free from pyrrol. It contained no aniline, but an amido-compound was evidently present, as a red colouration was obtained on adding a drop to a solution of furfurol and glacial acetic acid. In order to destroy amido-compounds, concentrated nitric acid was added to the oil in the cold. The red-brown solution was afterwards heated on the water-bath, poured into water, and distilled with steam. A small quantity of a heavy dark yellow oil (evidently a nitro-compound) passed over. The acid residue, after filtration, was saturated with 100 grms. of solid caustic potash, the oil which separated being extracted with ether, and the ethereal extract dried with caustic potash. On evaporation of the ether and subsequent distillation, 7 grms. of almost colourless oil resulted. The oil possessed the characteristic smell of pyridine, had a very bitter taste, and was strongly alkaline to litmus paper. White fumes were produced when vapour of hydrochloric acid was brought near it. The oil was fractionated twice, 10 fractions being taken between 140° and 250°. The greater part passed over at 165—185°. Each portion gave reactions with solutions of iodine in potassium iodide, tannic acid, picric acid, and mercuric chloride. Potassium ferrocyanide gave precipitates with several fractions. No distinct colourations were obtained with concentrated mineral acids. The fractions between 185° and 250° each contained 12·5 per cent nitrogen. The remaining fractions gave the following results:—

175—185° .. 0·1052 gave 11·6 c.c. moist nitrogen at 13° and 749 m.m.
165—175° .. 0·1171 gave 13·3 c.c. moist nitrogen at 15° and 749 m.m.
155—165° .. 0·1265 gave 15·3 c.c. moist nitrogen at 15·5° and 742 m.m.
140—155° .. 0·1991 gave 24·1 c.c. moist nitrogen at 16·5° and 741·5 m.m.

Fraction.	Nitrogen.		Calculated for—		
175—185°	12·84 per cent	collidine	$C_8H_{11}N$	11·57	per cent
165—175°	13·10 ,,	lutidine	C_7H_9N	13·09	,,
155—165°	13·78				
140—155°	13·75 ,,	picoline	C_6H_7N	15·05	,,

Analyses of various fractions of bases obtained in a similar manner from a different sample of bran gave the following results:—

180—200° .. 0·0916 gave 0·2632 CO_2 and 0·0780 H_2O.
0·0833 gave 8·6 c.c. moist nitrogen at 18·5° and 767·2 m.m.
170—180° .. 0·0890 gave 0·2555 CO_2 and 0·0746 H_2O.
0·1725 gave 0·4906 CO_2 and 0·1433 H_2O.
0·0713 gave 7·41 c.c. moist nitrogen at 15·5° and 751·7 m.m.
160—170° .. 0·0930 gave 0·2675 CO_2 and 0·0770 H_2O.
0·1644 gave 0·4746 CO_2 and 0·1304 H_2O.
0·1690 gave 18·4 c.c. moist nitrogen at 15° and 734·3 m.m.
140—160° .. 0·1747 gave 0·4918 CO_2 and 0·1370 H_2O.
0·1626 gave 0·4560 CO_2 and 0·1252 H_2O.
0·1461 gave 16·0 c.c. moist nitrogen at 15·5° and 762·7 m.m.
0·1161 gave 13·4 c.c. moist nitrogen at 15·5° and 737 m.m.

	Fraction 180—200°.	Fraction 170—180°.		Calculated. $C_8H_{11}N$.
C	78·35 per cent	78·26	77·56 per cent	79·34
H	9·46	9·31	9·23	9·09
N	12·08	12·00	—	11·57

	Fraction 160—170°.		Calculated.
	I.	II.	C_7H_9N.
C	78·43	78·72	78·50
H	9·20	8·83	8·41
N	12·30	—	13·09

	Fraction 140—160°.*		Calculated.
	I.	II.	C_6H_7N.
C	76 79	76·48	77·42
H	8·72	8·57	7·53
N	12·90	13·06	15·05

* This fraction was evidently not perfectly dry.

Several fractions were acidified with concentrated hydrochloric acid, an excess of a concentrated solution of platinum tetrachloride added, and the solution allowed to evaporate spontaneously. When the crystals ceased to increase in bulk, the mother-liquor was decanted, the crystals were washed with alcohol and ether, and dried at 100°. On analysis the platinum salts gave the results recorded in Table III.

200—225° gave a picrate as yellow microscopic arborescent crystals melting at 190—192°. The figures in this table conclusively prove the basic oil to contain picoline, lutidine, and collidine.

Treatment of the Non-basic Oil.

The oil which was unaffected by dilute hydrochloric acid weighed 173 grms. It yielded on distillation 166 grms. of oil boiling at 86—310°, about 145 grms. passing over between 150—280°; it contained 2 per cent nitrogen.* Bromine acted violently on the oil, white fumes (giving an acid reaction with litmus paper), a violet coloration, and a dark brown oil being produced. The whole of the oil was shaken several times with a solution of sodium bisulphite, and subsequently washed with water. The bisulphite extract was filtered, saturated with potassium carbonate, and the oil which separated extracted with ether. After drying and evaporating the ether, 4·5 grms. of oil boiling at 90—225° resulted on distilling. About 3·5 grms. dis-

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* The last drops gave a brilliant red colour on boiling with a pine splinter and dilute hydrochloric acid. Bromine acted violently on the oil, white fumes being produced, and on the excess of bromine being removed by a current of air, the mixture assumed an intense violet colour.

* Calculated as trimethylpyrrol would be about 15 per cent.

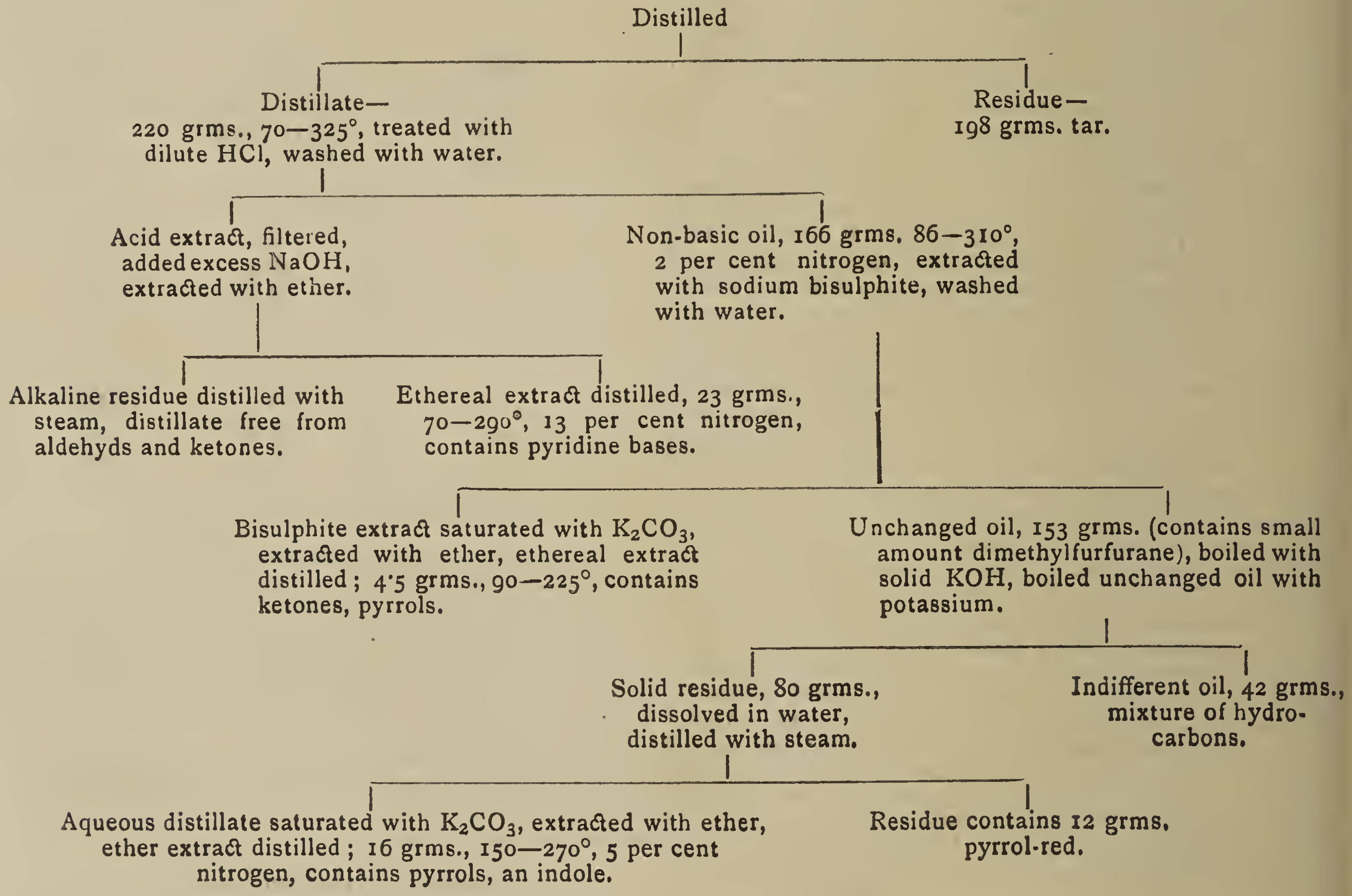
TABLE III.

Fraction 200—205° .. .. 0·1692 gave on ignition 0·0521 metallic platinum.
„ 165—175° .. .. 0·2037 „ „ 0·0641 „ „
„ 155—165° .. .. 0·1630 „ „ 0·0529 „ „

Fraction.	Pt salt.	Melting-point.	Platinum found.	Per cent Pt calculated. $(C_8H_{11}NHCl)_2PtCl_4$.	
200—205°	Red-brown dense masses of thick needles, silky lustre	190—191° decomposes.	30·79	30·12	(1)
165—175°	Dense masses of orange-red needles and square plates	181—183° decomposes.	31·47	$(C_7H_9NHCl)_2PtCl_4$. 31·47	(2)
155—165°	Similar to preceding fraction . ..	191—193° decomposes.	32·45	$(C_6H_7NHCl)_2PtCl_4H_2O$. 31·99	(3)
140—155°	Orange-red thick needles and square plates	185°	—	—	(4)

(1) α-Methylethylpyridine platinochloride melts at 190°.
(2) α-Ethylpyridine platinochloride melts at 164°.
(3) β-Picoline platinochloride (hydrated salt) melts at 191—195°.
(4) α-Picoline platinochloride melts at 178°.

TABLE IV.—THE OIL B, 418 grms.


Distilled

Distillate—220 grms., 70—325°, treated with dilute HCl, washed with water.

Residue—198 grms. tar.

Acid extract, filtered, added excess NaOH, extracted with ether.

Non-basic oil, 166 grms. 86—310°, 2 per cent nitrogen, extracted with sodium bisulphite, washed with water.

Alkaline residue distilled with steam, distillate free from aldehyds and ketones.

Ethereal extract distilled, 23 grms., 70—290°, 13 per cent nitrogen, contains pyridine bases.

Bisulphite extract saturated with K_2CO_3, extracted with ether, ethereal extract distilled; 4·5 grms., 90—225°, contains ketones, pyrrols.

Unchanged oil, 153 grms. (contains small amount dimethylfurfurane), boiled with solid KOH, boiled unchanged oil with potassium.

Solid residue, 80 grms., dissolved in water, distilled with steam.

Indifferent oil, 42 grms., mixture of hydrocarbons.

Aqueous distillate saturated with K_2CO_3, extracted with ether, ether extract distilled; 16 grms., 150—270°, 5 per cent nitrogen, contains pyrrols, an indole.

Residue contains 12 grms. pyrrol-red.

tilled between 125° and 215°. It contained 5·5 per cent nitrogen. Potassium acted violently on the oil. The solid product of the reaction was washed with ether and dissolved in water. The aqueous solution, on distillation, yielded a colourless oil which gave a well marked pyrrol reaction, and a white precipitate with mercuric chloride. Phenylhydrazin mixed with the oil became warm, and water separated on standing. A few drops of the oil, collected during the distillation at about 100°, gave a brilliant coloration with Bittó's reagent for methylpropyl ketone, and a violet coloration with a pine splinter and hydrochloric acid proved the presence of a homologue of furfurane.

The oil unaffected by sodium bisulphite weighed 153 grms. A portion of oil obtained in a similar manner from a former distillation of bran was proved in the following manner to contain dimethyl furfurane:—

100 grms. of oil, 1000 c.c. water, and 25 grms. of concentrated hydrochloric acid were heated in sealed tubes at 160° for six hours. The insoluble oil was filtered, and the claret-coloured filtrate saturated with potassium carbonate. A small quantity of a brown oil, smelling of acetonyl acetone, separated and was extracted with ether. The ethereal solution was dried with potassium carbonate, the ether evaporated, and the remaining oil distilled. About 0·6 grm. of nearly colourless oil boiling at 170—

195°, mostly at 185—190°, passed over.* This portion was mixed with 0·8 grm. potassium carbonate and 0·8 grm. hydroxylamine hydrochloride and dissolved in the least possible quantity of warm water for solution. Crystals separated on allowing the solution to stand. A small quantity of brown oil being also present, the whole was warmed until the crystals dissolved, and the oil filtered off; the latter gave a strong pyrrol reaction. The crystals which were deposited from the filtered solution were recrystallised from a small quantity of water; the purified crystals were in clusters and just tinged pink. After filtration and drying on the water-bath, 0·17 grm. of crystals melting at 132—133° were obtained.†

0·1404 gave 23·3 c.c. moist nitrogen at 16° and 757·2 m.m.
Nitrogen, 19·27 per cent $C_6H_{12}N_2O_2$. Calculated, 19·45 per cent N.

Treatment of the Oil which was Unchanged by Sodium Bisulphite.

An attempt was made to separate the pyrrols in the form of potassium salts from the oil unaffected by sodium bisulphite, by long-continued boiling with solid caustic potash. Ammonia was evolved, and the oil several times decanted from the brown solid products and treated with more potash. When no further action took place the oil was boiled repeatedly with potassium. The solid products of the reactions were separated from the fused potash and the potassium respectively. They amounted to about 80 grms., and after washing with ether constituted a brown powder which took up moisture with avidity and quickly became oily. The mass was dissolved in water and distilled with steam. The residue in the still gave on filtration about 12 grms. of pyrrol red. The aqueous distillate mixed with oil was extracted with ether. About 16 grms. of oil boiling at 150—270° resulted. The portion boiling at 150—160° contained 5 per cent nitrogen. The oil was found to be a mixture containing pyrrols and indols, as, besides having the characteristic smell of the latter, it gave Beyer's reaction for indole. Various fractions of the oil were tested separately, and the lower ones gave the following reactions for pyrrols:—Boiling with a solution of isatine in glacial acetic acid caused a blue colouration: phenanthraquinon in glacial acetic acid gave a violet colouration on adding dilute sulphuric acid and chloroform. The last drops from the distillation at about 270° did not give these colourations, but exhibited Fischer's pine-splinter reaction for indole.

The oil which was unaffected by potassium was washed with dilute hydrochloric acid and dried. It still contained 1 per cent nitrogen, and gave a red colour on boiling with a pine-splinter and hydrochloric acid. On distilling, 2 grms. boiled at 80—150° and 40 grms. at 150—300°. The portion boiling at 80—150° yielded on nitration a heavy yellow oil, resembling in smell and appearance nitrobenzol, which, on reducing with tin and hydrochloric acid, gave the reactions for aniline. Ten grms. of fraction 150—300° were dissolved in ether, and excess of bromine added in the cold. A few white fumes were given off. A violet coloration was produced, and the solution turned brown later. After washing out the excess of bromine with dilute sodium hydrate solution, the oil (weighing 16 grms.) was distilled with steam. The aqueous distillate contained a heavy yellow oil, which, on extraction with ether and subsequent drying, weighed 8·5 grms. It had a fragrant smell and distilled with partial decomposition at 185—235°.

The remaining 30 grms. of fraction 150—300° was shaken with cold concentrated sulphuric acid. No rise of temperature was noted. After standing twenty-four hours, the mixture was gently heated on a sand-bath, using a reversed condenser. Sulphur dioxide was evolved and carbon separated. The mass was distilled with steam and the insoluble oil which passed over extracted with ether, dried, and, after evaporation of the latter, treated with Nordhausen sulphuric acid until no further action. The unchanged oil was washed, dissolved, in ether, dried, and distilled. About 3 grms. of a mobile colourless oil, smelling like petroleum, distilled over between 190—275°; the specific gravity at 21° was 0·77. From these reactions it is evident the 42 grms. of indifferent oil consisted for the greater part of olefines mixed with paraffins and aromatic hydrocarbons. (See Table IV.).

Summary of Results.

The following substances were separated from the aqueous distillate:—

A.

About 300 grms. of ammonia as chloride.
" 20 " amine bases as salts (methylamine, ethylamine, and trimethylamine).
" 26 " oil containing pyrrol and its homologues (and averaging 11 per cent nitrogen).
" 29 " ketones (methylpropyl ketone) and small quantities of ethyl alcohol.
Traces of furfurans, pyridine bases, and indoles.

The Oil B yielded:—

About 10 grms. of pyridine bases (picoline, lutidine, collidine) and small quantities of amido compounds.
Small amounts of ketones and dimethyl furfurane.
16 grms. of pyrrols mixed with an indole.
42 grms. of indifferent oil, consisting chiefly of olefines and lesser quantities of paraffins and aromatic carbons.

The substances obtained by the extraction of bran with ether and other solvents are now being investigated.

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SODIUM CHLORIDE AT HIGH TEMPERATURES.

By ROBERT MELDRUM, F.C.S.

Some years ago a series of experiments was made in connection with the production of salt vapour, during which I observed that the molten salt was sometimes faintly alkaline, and that the vapour had nearly the same smell as strong hydrochloric acid, but not quite so pungent. This could not be accounted for otherwise than by assuming that the salt underwent decomposition in the absence of aqueous vapour. To settle this question the following experiments were made, which seem to demonstrate that sodium chloride in the absence of water does not form any alkali, even in the presence of the substances enumerated below, with the exception of iron peroxide:—

1. Pure NaCl, kept molten for five minutes over blowpipe, when cold, boiled out with alkali-free distilled water, which gave a distinct alkaline reaction with phenolphthalein.
2. Four grms. of the unfused salt, dissolved in 20 c.c. water, gave slight alkaline reaction.
3. Saturated 5 grms. of the unfused NaCl with pure HCl, so as to neutralise any alkali present, expelled acid by heating, and melted over blowpipe in platinum crucible. The cold fusion was extracted with alkali-free water, a distinctly alkaline reaction being the result.
4. Two samples of commercial salt were melted, but yielded a neutral solution.
5. Ten grms. of pure NaCl were saturated with pure HCl, dissolved in NH_3-free water, boiled, and evaporated to dryness; repeated this till no result was given with

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* Acetonylacetone boils at 188°.

† Acetonylacetone dioxime melts at 135°. The above method of Paal (*Ber.*, xviii., 59) for the determination of dimethylfurfurane by splitting the furfurane ring by means of dilute acid, and the formation of the dioxime from the resulting γ-diketone is applicable to other homologues of furfurane (Laycock, "Inaug. Diss.," Würzburg, 1889).

methyl-orange. Finally, evaporated to dryness, and melted for fifteen minutes in platinum crucible in muffle, and when cold extracted the mass, but gave no trace of alkali. This was repeated several times with the same result.

6. Eight grms. pure NaCl + 8 grms. clay, fused in platinum crucible in muffle at white heat. The resultant mass on treatment with water gave no indication of alkali.

7. Fused 8 grms. NaCl + 8 grms. Fe_2O_3 (both alkali-free) over blowpipe in platinum crucible; distinct reaction for alkali.

8. A mixture of 8 grms. NaCl + 8 grms. Fe_2O_3 (both pure and alkali-free), fused in clay crubible in muffle for two hours at yellow heat; no trace of alkali. In this case the crucible was found, after boiling in water, to be lightly glazed inside, thus showing an action had taken place, and that the free alkali had been absorbed by the clay.

9. Fused 8 grms. NaCl + 8 grms. SiO_2 (both pure and alkali-free) in clay crucible in muffle. No trace of alkali present. On boiling the crucible it showed no evidence of having been glazed inside. However, any alkali liberated may have combined with the SiO_2 to produce a neutral salt. The same experiment repeated in a platinum crucible gave the same result.

10. When 8 grms. NaCl + 8 grms. pure plumbago dust were submitted in muffle to a white heat, the fused mass, on extracting with water and filtering, gave no result for traces of alkali.

11. Melted common salt and MnO_2 in platinum crucible over blowpipe. Fusion gave no reaction with phenolphthalein, or indication of the presence of manganates or permanganates.

12. When salt is kept molten at white heat in covered clay crucible for some hours, there is always evolved a dense white vapour which smells very like strong HCl gas, but does not act upon moist blue litmus-paper, and the melt gives no indication of alkali. The crucible when broken up and boiled showed no internal glaze. From this I assume that salt vapour has nearly the same smell as HCl.

THE COLOUR OF SULPHUR VAPOUR.*

By JAS. LEWIS HOWE and S. G. HAMNER.

Our attention was some time since called to a curious difference of opinion on the part of chemical authorities as to the colour of sulphur vapour. In twenty-nine standard text-books and reference books examined which mention the colour of the vapour, thirteen different colours are given, as follows:—

	Authorities.
Deep yellow	4
Orange	5
Orange to dark yellow	1
Orange-yellow	2
Brownish yellow	6
Yellowish brown	1
Amber	2
Yellowish red	1
Red	1
Deep red	2
Deep red to brown	1
Brownish red	2
Reddish brown	1

In no work was any mention found of a change in the colour of the vapour with changing temperature.

In order to examine the true colour of the vapour a number of experiments were carried out, which, while not complete or entirely satisfactory, nevertheless throw some light on the discrepancies cited. The first apparatus used consisted merely of a small test-tube of hard glass, within a larger tube, also of hard glass, the smaller tube being held free from contact with the larger by means of a wire frame. The ends of both tubes were stopped with asbestos wads to prevent free circulation of the air. A piece of roll sulphur was placed in the inner tube and heated by Bunsen burners. The pure sulphur vapour could be seen in the inner tube, the hot air in the outer tube preventing the condensation of the vapour on the sides. This simple apparatus gives a good view of sulphur vapour up to the softening point of the glass. The second form of apparatus used was a porcelain tube 2 c.m. in diameter and 16 c.m. long, with the ends covered by thin sheets of mica, and the whole tightly packed in a larger iron tube by clay. The inner tube was thus not sealed perfectly, but permitted the escape of the excess of sulphur vapour on heating, though under some considerable pressure. The apparatus was heated in a muffle whose rear end was replaced by a sheet of mica. It was thus possible to have a clear view through the tube while it was heating. The temperature was gauged approximately by tubes of silver chloride (melting-point 457°), lead chloride (melting-point 498°), and potassium iodide (melting-point 634°).

In every case the sulphur, when just beginning to boil, gave a vapour which would perhaps be denominated orange-yellow. This colour is almost exactly matched by a normal solution of potassium bichromate. As the temperature increases the colour very rapidly deepens, and loses every vestige of the yellowish tint. This corresponds to a temperature not much above 457°. On raising further the temperature, the colour deepens further. The deepest colour was found, by several experiments, to be at the temperature of about 500° (lead chloride just fused). The paler red colour is matched by a solution consisting of—

	Parts.
Ferrric chloride (normal solution)	1
Potassium thiocyanate (normal solution)	2
Water	312

The deepest red is matched by a solution—

	Parts.
Ferric chloride (normal solution)	1
Potassium thiocyanate (normal solution)	2
Water	250

This is as far as the changes can be observed in the test-tubes. Heated in the muffle, immediately above 500°, the vapour begins to grow perceptibly lighter, at 634° being almost straw-colour. Up to this temperature the escaping jet of sulphur vapour indicated that the tube must be filled with sulphur vapour. When this jet ceased the results became too doubtful to record. That the rapidly decreasing intensity of colour was not due merely to decreasing pressure is evidenced by the fact that the colour of the vapour at its darkest point was almost exactly the same in the porcelain tube and in the test-tube, in the latter case the vapour being practically at atmospheric pressure.

The cause of the different colours applied to sulphur vapour is doubtless due to three causes:—

1. The general difficulty of describing the colours of vapours, the relative intensity of which is so much less than that of our ordinary standards.

2. The fact that the colour of sulphur vapour varies with the temperature.

3. Sulphur vapour condenses so readily that when boiled in a test-tube the sides of the tube are covered with a layer of the brownish-red liquid, which has doubtless sometimes been mistaken for the vapour. Similarly, when sulphur fumes escape from a hot covered crucible into which sulphur has been thrown, it is the condensing sulphur mist, very deep red in colour, which one sees, and not the true vapour of sulphur.

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* Read at the Boston meeting of the American Chemical Society, August, 1898. From the *Journal of the American Chemical Society*, vol. xx., No. 10.

The conclusions of this paper are that the colour of sulphur vapour varies with the temperature, being of an orange tint just above its boiling-point, deepening to a red which is strongest at 500°, and then becoming rapidly lighter with increasing temperature. The colour at the boiling-point is that of a normal solution of potassium bichromate; that of the deepest red is that of a rather dilute solution of ferric thiocyanate.

It is hoped it may be possible to carry these experiments further, but no reservations are made of the subject if others are interested.

THE COLORIMETRIC ESTIMATION OF SMALL AMOUNTS OF CHROMIUM,

WITH SPECIAL REFERENCE TO

THE ANALYSIS OF ROCKS AND ORES.*

By W. F. HILLEBRAND.

Introduction.

Having occasion to analyse a number of highly titaniferous magnetites containing chromium, phosphorus, and vanadium, it became a serious problem to effect satisfactory separations of all these bodies in a form fit for separate determinations. The method of T. Fischer ("Inaugural Dissertation," Rostock, 1894)—digestion of the precipitated lead salts with a strong solution of potassium carbonate—appears to offer the long-needed satisfactory quantitative separation of arsenic, phosphorus, chromium, tungsten, and molybdenum from vanadium, the normal lead meta-vanadate remaining quite unattacked, according to the author, while the other lead salts are wholly decomposed, but the applicability of this method to the separation of the minute amounts often found in rocks and ores has not been tested. The time required is considerable, hence it was desirable to devise a more rapid way for determining both chromium and vanadium without resorting to this separation. That this object has been measurably achieved, with certain limitations as to vanadium, the work thus far done seems to indicate. The present paper will deal only with the rapid estimation of chromium either in absence or presence of any or all of the elements above mentioned.

In view of the high colouring power of the chromates, it is surprising that this property does not seem to have been made the basis for a quantitative method for the estimation of chromium. A search through some of the more important text-books has revealed no reference to such a method, and I am unaware that one has even been suggested. Yet the results attainable by colorimetric comparisons of dilute alkaline solutions of unknown strength with those of a known standard, leave little to be desired in point of quantitative accuracy.

As with colorimetric methods in general, this one gives better results with small than with large percentages of chromium, yet it can be applied in the latter cases with very fairly satisfactory results by making a larger number of consecutive comparisons with the same solution.

Outline of Method.

The chromium is brought into a measured volume of solution as monochromate, rendered alkaline by sodium carbonate, and the whole or a portion of this solution is then compared with a definite amount of a somewhat stronger standard likewise made alkaline with sodium carbonate. The latter is diluted with water till both seem to be exactly alike in colour, when a simple calculation gives the amount of chromium sought. The actual comparison takes little time, and any number of repetitions can be made if desired in order to secure greater accuracy from the mean of a large number of observations. The preparation of the solution to be tested offers nothing novel, but certain precautions have to be observed therein as well as in the colour comparisons, which will be touched upon later.

Testing of Method by Comparison of Standard Solutions.

Two standard solutions were prepared by dissolving 0·25525 and 0·5105 grm. potassium chromate in 1 litre of water made alkaline by a little sodium carbonate, each cubic centimetre then corresponding respectively to one-tenth and two-tenths m.grm. chromic oxide, in which latter form chromium is usually reported in rocks and ores. Definite amounts of one of the standards were then diluted with varying amounts of water in a tall square glass vessel with exactly parallel sides. Into an exact duplicate of this vessel 5 or more c.c. of the standard were introduced from a burette and diluted with water from another burette till exact agreement seemed to be reached on looking through the glasses horizontally.

In the accompanying tables are recorded all observations, without regard to the sequence in which they were made. No greater pains were taken to get exact agreement of colour than are ordinarily observed in our routine titanium estimations, which are carried out in a precisely similar manner, so that the results may be taken to represent every-day work without extreme precautions. In only two cases can the observations be considered really bad, viz., the third comparison of No. 6 and the first of No. 16.

The first table and the grand mean show an apparent personal tendency toward slightly high results, though it is possible that this is due to a slight difference in the internal dimensions of the two glasses, the same one always having been used for the standard solution. If this is so, a long series of tests with glasses reversed should give a general mean slightly below 100.

Testing the Method on Ores and Rocks.

In order to prove the value of the method in rock analysis, varying amounts of the standard solution were evaporated in a large crucible with 5 grms. of an iron ore carrying phosphorus and vanadium, and fused with 20 grms. of sodium carbonate and 3 grms. sodium nitrate. The aqueous extract, after reduction of manganese by methyl or ethyl alcohol, was nearly neutralised by nitric acid and evaporated to secure approximate separation of silica and alumina. As a precautionary measure, since a little chromium is usually carried down, the precipitate was ignited, silica was removed by hydrofluoric and sulphuric acids, the residue was fused with sodium carbonate, and alumina again separated as before. To the combined filtrate was added mercurous nitrate and the slightly washed copious precipitate of phosphate, chromate, vanadate, and carbonate of mercury was ignited with the paper in a platinum crucible, which can be done without much fear of loss or injury to the crucible. The residue was then fused with a little sodium carbonate, extracted with water, filtered into a graduated flask, and made up to 50 or 100 c.c., according to the intensity of the colour, and compared with the standard. A similar operation was carried out with a silicate rock. Table III. shows the results.

When the percentage of chromic oxide in an ore or mineral is more than about two-tenths per cent, and vanadium has not also to be estimated, much time may be spared by at once taking the colour of the original extract from the sodium carbonate fusion, after ensuring complete reduction and removal of manganese, and perhaps concentrating. But if the chromium is much less than this amount, and especially if several grms. of powder have been operated on, it becomes difficult or impossible to obtain a filtrate of sufficiently small bulk to show a decided colour. Therefore, in such cases, and when vanadium is likewise to be estimated, it is necessary to precipitate as above with mercurous nitrate in order to eventually have

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* Read before the Washington Section, March 10, 1898. From the *Journal of the American Chemical Society*, xx., No 6, June, 1898.

Table I.

Ten c.c. standard represent one m.grm. chromic oxide.

No.	Test solution.		Comparison standard.		Contents, as chromic oxide.	Chromic oxide found.	Chromic oxide present.	Error.	Chromic oxide found.
	Standard.	Diluted with water.		H_2O added.					
	C.c.	C.c.	C.c.	C.c.	M.grms.	M.grms.	M.grms.	M.grm.	Per cent.
1.	10*	90*	5	44·00	0·5	0 98	1	−0·02	98·0
2.	20†	80†	5	21·00	0·5	1·92	2	−0·08	96·0
3.	40	60	10	14·60	1·0	4·06	4	+0·06	101·5
4.	40	60	9·7	14·25	0·97	4·05	4	+0·05	101·2
			10	13·95	1·0	4·17	4	+0·17	104·4
			10	14·30	1·0	4·11	4	+0·11	102·9
			10	14·20	1·0	4·13	4	+0·13	103·3
5.	40	60	10	14·65	1·0	4·05	4	+0·05	101·4
			10	15·65	1·0	3·90	4	−0·10	97·5
6.	40	60	10	15·25	1·0	3·96	4	−0·04	99·0
			10	14·30	1·0	4·11	4	+0·11	102·9
			10	13·15	1·0	4·32	4	+0·32	108·0
			10	14·75	1·0	4·04	4	+0·04	101·0
			20	29·50	2·0	4·04	4	+0·04	101·0
7.	50	50	10	9·75	1·0	5·06	5	+0·06	101·2
8.	50	50	10	10·00	1·0	5·00	5	0·00	100·0
9.	60	40	10	7·20	1·0	5·81	6	−0·19	96·7
10.	75	25	20	6·65	2·0	7·505	7·5	+0·005	100·1
			20	6·60	2·0	7·519	7·5	+0·019	100·2
			10	3·15	1·0	7·605	7·5	+0·105	101·4
			15	4·70	1·5	7·610	7·5	+0·11	101·5
11.	10	10	10	10·15	1·0	0·992	1	−0·008	99·2
			20	19·75	2·0	1·006	1	+0·006	100·6
12.	10	11	10	10·60	1·0	1·02	1	+0·02	102·0
13.	14·2	26·9	10	18·60	1·0	1·43	1·42	+0·01	100·7
			20	35·70	2·0	1·47	1·42	+0·05	103·5
14.	15	24·35	10	16·55	1·0	1·48	1·5	−0·02	98·7
15.	16	20	10	13·30	1·0	1·54	1·6	−0·06	96·2
			20	24·30	2·0	1·63	1·6	+0·03	101·9
16.	31·9	20·6	10·5	8·10	1·05	2·96	3·19	−0·23	92·8
			20·5	14·20	2·05	3·10	3·19	−0·09	97·2
17.	62·05	22·3	20	7·00	2·0	6·25	6·205	+0·45	100·7
			40	12·00	4·0	6·49	6·205	+0·285	104·6

Mean percentage found, 100·5.

* Colour in this dilution too faint.

† Limit of dilution for clear distinction of colour in a thickness of three and three-tenths c.m.

Table II.

Varying amounts of Standard No.2 (1 c.c. = 0·2 m.grm. Cr_2O_3) diluted till of the same concentration as Standard No. 1.

No.	Standard.		Contents as chromic oxide.	Chromic oxide found per 100 c.c.	Chromic oxide present in 100 c.c.	Error.	Chromic oxide found.
		Water added.					
	C.c.	C.c.	M.grms.	M.grms.	M.grms.	M.grm.	Per cent.
18.	5	5·2	1	9·80	10	−0·2	98·0
19.	10	9·95	2	10·02	10	+0·02	100·2
20.	15	15·8	3	9·74	10	−0·26	97·4
21.	20	20·0	4	10·00	10	0·00	100·0
22.	30	29·5	5	10·08	10	+0·08	100·8

Mean, 99·3. Grand mean, 100·36.

Table III.

	Chromic oxide added.	Chromic oxide found.
	M.grms.	M.grms.
I. 5 grms. iron ore	7·03	7·18
	—	7·20
	—	7·25
	—	7·21
II. 5 grms. iron ore	2·99	3·08
	—	3·13
III. 2 grms. silicate	1·6	1·53
	—	1·57
	—	1·59

a small bulk of sufficiently coloured solution. Even then, for very minute amounts, it is necessary to use Nessler tubes exactly as in ammonia estimations.

If nitre has been used in the fusion and the crucible has been attacked by it, a yellow colour of the filtrate may be due to dissolved platinum, but neither the proportion of nitre nor the temperature of the blast should ever be high enough to permit the crucible to be attacked.

(To be continued).

Agricultural Exhibition at Warsaw.—An Agricultural Exhibition will be held in the Museum of Trade and Agriculture, at Warsaw, from November 28th to December 5th, 1898.

THE TRANSITION TEMPERATURE OF SODIC SULPHATE, A NEW FIXED POINT IN THERMOMETRY.[*]

By THEODORE WILLIAM RICHARDS.

I. *On the Constancy of the Point in Question.*

With the assistance of Jesse Briggs Churchill.

According to the Phase Rule of Willard Gibbs, in order to obtain a nonvariant point in any system two more conditions must be definitely fixed than the number of components in the system. In other words, if the system contains only one component, three conditions must be fixed; if two components, four conditions, and so on. Since such a nonvariant[†] point is invariable in temperature, as well as in every other respect, there evidently exist a great number of definite temperatures obtainable by the combinations of different substances.

Of these multitudinous nonvariant points the world uses only two, the simplest possible, as the standards of thermometry. The fixed conditions are:—a definite pressure, and two phases of one component, water. While undoubtedly 0° and 100° C. will always remain the standards of reference, it would be extremely convenient to have at least one definitely determined point between these. Many thermometers do not cover this whole range, and all are noticeably upset as to their internal condition by such wide variations of temperature.

Landolt's very carefully made determinations of the melting-points of a number of organic substances (*Zeitsch. Phys. Chem.*, 1889, iv., 349) showed that these bodies are too much subject to contamination with clinging impurities to serve as accurate standards. Organic compounds are too plentiful in number to make the easy obtaining of any one alone an easy matter, and among inorganic substances no single suitable substance beside water seems to exist.

There is no reason, however, why we should be confined to the use of a single component in this search for fixed points. Two components, requiring four fixed conditions, should answer equally well. The only essential is that the substance involved should form perfectly definite phases, and should be capable of being obtained in the pure state. Nernst has suggested the use of "cryohydric" points as a means of maintaining constant low temperatures, but the possibility of utilising higher nonvariant points involving two components as a basis of thermometry and a means of maintaining constant temperature does not seem to have been generally realised.

Of the many pairs of substances which might serve the purpose in view, the pair, sodic sulphate and water, seems to be the most suitable for several reasons.

In the first place, the system ($Na_2SO_4 + Na_2SO_4 \cdot 10H_2O$ + saturated solution + vapour) is in equilibrium at 32·5° (Lowenherz found 32·39°, *Zeitschr. Phys. Chem.*, xviii., 70)—a most convenient point, less above ordinary temperatures than 0° is below them, and within the field of even very large-bulbed thermometers. This small elevation involves very little disturbance in the tension of the glass, as well as very slight correction on account of the column projecting into the cooler atmosphere of the room. Moreover, 32·5° is near the temperature of greatest difference between the hydrogen and the mercury thermometer.

On the other hand, sodic sulphate does not "melt" so easily as to cause any difficulty in keeping it unfused in a reasonably warm place. A substance melting only a few degrees lower would be continually freezing into a solid lump, which could be extracted from its bottle only by melting. The fact that it is not deliquescent is also of value.

A much more important advantage, as far as exactness is concerned, is to be found in the great ease with which the substance may be obtained in a pure state. Its solubility is far less at 10° than it is at 33°—hence its recrystallisation by cooling does not involve much loss. Moreover, it may also be crystallised in the anhydrous state by simply melting the aqueous crystals; and since this process necessarily brings into play a wholly new set of isomorphous relations, it may be relied upon to eliminate impurities which are not rejected by the hydrated crystals.

Again, the "melting" absorbs enough heat to insure the rendering "latent" of any heat evolved by the mechanical process of gentle agitation, or of any heat taken in from the environment. The semi-opaque nature of the mixture removes any serious danger from radiant heat.

Since the volume scarcely changes with the transition, reasonable alterations in pressure do not cause any essential change in the temperature. This fact may be of importance if one has occasion to use very deep layers of the mixture.

The number of possible hydrates is smaller in this case than in many, hence the change is a sharp one. The salt $Na_2SO_4 \cdot 7H_2O$ is so soluble that it cannot exist in the presence of the other solid phases.[*]

Last, but not least, Glauber's salt is extremely inexpensive, and at hand in every chemical and physical laboratory. Oddly enough, the melting-point of the anhydrous salt, 865°, is one of the most satisfactory standards among high nonvariant temperatures.

It is needless to state that the usual precautions necessary to obtain accurate results were taken in the thermometric work which follows, as well as in the chemical preparation. Several thermometers were used in the course of the experiments; they will be described as the account progresses. For the first determinations, which were wholly of a relative nature, a Beckmann thermometer of the first quality, made by Goetze, of Leipzig, was chosen. This instrument was graduated to hundredths of a degree, and could be easily read to within a thousandth. Because of the thinness of its bulb, this thermometer was especially sensitive to pressure; hence it was guarded carefully during its use. It was always read in a vertical position, as were all the other thermometers. Since the temperature of the room remained essentially constant during the preliminary experiments, the barometric pressure did not change by important amounts, and the height of the mixture around the bulb was always about the same, the readings are directly comparable with one another without correction.

First Problem.—The Effect of the Temperature of the Environment.

At first sodic sulphate prepared by crystallising twice in a porcelain dish the ordinary "purissimum" material of commerce was used. This preparation was coarsely powdered and partly dried in a desiccator. When placed in a wide test-tube surrounded by a Beckmann air-jacket (a still wider test-tube), and allowed to remain for an hour in a thermostat at 32·9°, it melted with absolute constancy at a temperature indicated on the arbitrary scale by 4·758. On the following day, upon being replaced in the thermostat the "melting" point appeared to be precisely the same. It was found advantageous to melt the crystals partially into a pasty mass, by means of a gas-lamp, before immersing them in the thermostat, and the mass was stirred

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[*] From the *American Journal of Science*, vol. vi., 1898; also *Zeitschr. Phys. Chem.*, xxvi., 691.

[†] Trevor's term "nonvariant" is a peculiarly happy selection. His similar terms, "monovariant," &c., would be equally suitable if they were not hybrids of Greek and Latin. Would it not be well to use, instead of these, the homogeneous words "univariant," "bivariant," &c.? These latter terms are not likely to cause trouble because of their similarity to "univalent," &c., for both the numbers of syllables and the accents are different in the two series.

[*] The non-existence of the substance $Na_2SO_4 \cdot H_2O$ may now be considered proved. Even if it really exists, however, the facts recorded below remain: one must merely read "monohydrated" instead of "anhydrous," and the theory will be unchanged. See de Coppet, *Berichte d. D. Ch. Gesell.*, xii., 248; also, Lescœur, *Ann. Chim. Phys.*, 1890, [6], xxi., 526

gently by a ring-shaped platinum stirrer. Upon raising the temperature of the bath to 36° not the least change was observed, although this application of a higher temperature was allowed to continue for half an hour. A lower temperature, on the other hand, had a less satisfactory effect. When the bath was kept at 29° the thermometer in the sodic sulphate indicated a constant reading of 4·746, a depression of 0·012°. In order to verify this phenomenon, a purer specimen, which melted at 4·760° with the bath about 33°, was surrounded by an environment at 30°, and then indicated 4·750° on the arbitrary scale.

Thus it is evident that the most satisfactory results are to be obtained by melting the salt slowly, and not by allowing it to solidify. The reason for this is obvious. The anhydrous salt is far less apt to form supersaturated solutions than the hydrated salt, and the crystals instantly melt upon being heated above their transition point, absorbing an appreciable amount of heat in the process. On the other hand, in order that the mass may solidify, the anhydrous mass must dissolve while the supersaturated solution is depositing its hydrate, both of these operations being much less prompt than the preceding. In all subsequent determinations the thermostat was kept about half a degree above the point sought, and it was found that the mixture would then melt so slowly as to last for hours.

Second Problem.—Concerning the Purity of the Salt Required.

Löwenherz (*loc. cit.*) has found, under van 't Hoff's direction, that an admixture of foreign substances lowers the transition temperatnre of sodic sulphate just as it does simpler melting-points. Hence a study of the purification of the salt is of great importance for our present purpose.

The mother-substance used in preparing the salt above was found to melt at a temperature of 0·06° below that which had been twice re-crystallised in porcelain. Four further crystallisations in platinum vessels changed the transition temperature only 0·002 above that corresponding to two re-crystallisations, the arbitrary scale indicating 4·760°.

While it seemed probable that this re-crystallisation had freed the salt from anything which could affect its melting-point, further proof seemed proper. Hence a kilogrm. or so of pure sodic hydric carbonate was thoroughly washed with pure water, and was then dissolved in an excess of pure dilute sulphuric acid. After six crystallisations the salt was still perceptibly acid to methyl orange, and hence after testing the melting-point the salt was re-crystallised again, collected on a large Gooch crucible, and washed. Although now free from any trace of acid, it was precipitated as anhydrous salt by heating to 100° (the mother-liquor being rejected), re-dissolved at 33°, and re-crystallised by cooling. These final operations were conducted with the purest water and all the precautions necessary in the most refined work. A portion of the later mother-liquors was neutralised with pure soda and twice re-crystallised in order to obtain a third sample.

Another thermometer was used in testing the melting-points of these three samples. This thermometer, admirably made by Baudin of Paris, in 1880, is graduated to the fiftieth part of a degree, and can be read by means of a telescope and micrometer to within a thousandth. Its scale is about 40 c.m. long, and covering the twelve degrees between 21° and 33°, including the zero point below a small auxiliary bulb. This small bulb was always in the thermostat, leaving only about 10° of the column to be corrected for the lower temperature of the room. Following are the uncorrected results obtained with this thermometer:—

The slightly acid salt melted at	32·520
The neutralised and re-crystallised salt melted at	32·560
The purest, nine times re-crystallised salt melted at..	32·561
The twice re-crystallised salt first made melted at	32·560

The last observation was made in order to compare this series with the other which has been made with the Beckmann thermometer. As the pressure had increased since the other readings were taken, the arbitrary thermometer itself could not be satisfactorily compared with that of French manufacture.

Evidently it is a matter of no great difficulty to obtain sodic sulphate of constant "melting-point." Even two re-crystallisations of the purest Glauber's salt of commerce carried on in porcelain vessels seemed to be enough to eliminate any serious impurity. In order to obtain certain results, the purification should be continued until the melting-point is constant. The repeated re-crystallisation of the slightly acidified salt is especially instructive in this regard, for it is safe to conclude that when the acid has gone other accidental impurities would have disappeared also; and the methyl-orange test is one of extreme delicacy if the solution is not too concentrated.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, October 28th, 1898.

Mr. Shelford Bidwell, President, in the Chair.

A paper was read by Mr. W. R. Pidgeon, on "*An Influence Machine.*"

The machine, which was exhibited, consists of a pair of glass discs, rotating in opposite directions upon a spindle. They are partially covered on one face with narrow radial sectors of tin-foil, each provided with a small brass knob. This face of the disc, including its sectors, is then coated with insulating wax, leaving only the knobs projecting through the wax. Two earthing-brushes pass through two insulated fixed inductors, and support them. The inductors are kept charged by exploring-points connected to each, and placed so as to collect electricity from the revolving discs. By means of brushes, the sectors on each of the discs are successively earthed at the moment they pass the fixed inductors, *i. e.*, at the moment that their capacity is a maximum; and they are made to deliver up their charge to the main collecting brushes at the moment when they are electrically farthest from the inductors, *i. e.*, when their capacity is a minimum. Hence, if there is no loss of electricity in the process, the potential at the collecting brushes is proportionally high. Each sector of a particular disc, as it moves away from its inductor with rising potential, induces a corresponding potential on the sectors opposed to it on the second disc; this action is cumulative. The thick coating of wax restricts leakage to the small area of the contact knobs, so that surface effects of dirt and moisture are minimised.

Capt. J. H. Thomson, R.A., said that, apart from its electrical merits, the machine possessed advantages in mechanical construction. He thought there was still room for improvement in this respect. The counter-shaft should be done away with, and ball-bearings should be introduced. The inductor was a distinct improvement;

he thought the efficiency might be increased by adding other inductors. Platinum-iridium was the best material for brushes of such machines.

Prof. **Ayrton** asked what efficiency was obtained with modern influence machines in general.

Capt. **Thomson** had found that when running a machine by a motor, about 80 per cent of the power was wasted in mechanical friction; of the remaining 20 per cent a great deal was lost as electrical leakage.

Prof. S. P. **Thompson** thought it had been pointed out by Mr. Wimshurst that influence machines did not work well unless there were at least two thicknesses of glass between the inducing and induced conductors. That was why Mr. Wimshurst put his sectors on the outer faces of the glass discs. Mr. Pidgeon had departed from this. The advantage of the narrow spacing of the sectors was not very apparent.

Mr. **Wimshurst** (abstract of communication). Waxing the discs reduces leakage and increases the output; the wax-coating virtually doubles the number of plates. Inductors contribute a further increase to the output. In 1883 Mr. Wimshurst tried thick coatings of shellac, and also, duplicating the glass, with in some cases sectors upon the second glass to increase the capacity. The output was increased, but the construction lost simplicity. The indifference of Mr. Pidgeon's machine to dirt and dust was a most valuable result.

Mr. **Pidgeon**, in reply, showed a set of secondary inductors such as Capt. Thomson had just proposed. They improved the output by about 15 per cent, but they were troublesome to keep in order, for they increased the tendency to "reverse."

Dr. S. P. **Thompson** then repeated an experiment, discovered by Prof. Righi, on "*A Magneto-optic Phenomenon.*" It was originally described in *Roma*, *R. Accad. Lincei*, Atti. 7, Ser. 5, 1898.

A substance absorptive of light is submitted to a powerful magnetic field between the pole-pieces of an electro-magnet. The pole-pieces are drilled so that a beam of light from an arc-lamp can traverse the gap *along* the magnetic lines. A polarising prism is placed between the arc-lamp and the electro-magnet. After having passed through the magnetising apparatus, the beam thus polarised is examined by an analyser. The analyser must be turned to "extinction" before the magnetising current is turned on. If this is done, brightness is restored at the analyser as soon as the magnetic field is established. The substance absorbing the light in the gap may be nitric oxide fumes, or an ordinary spirit-lamp sodium flame. The second effect to be noticed is that when the emergent beam is examined there is a splitting of the lines. Righi explains this by supposing that when light of frequency, n, is brought into a magnetic field and passed *along* the lines of the field, it is split up into two sets of circular waves, a right-handed and a left-handed set, one of which sets is accelerated and the other retarded. There are now two frequencies, n_1, n_2, one a little higher and the other a little lower than n. But since the analyser is adjusted to extinguish n, there is brightness for n_1, n_2. Normally, nitric oxide absorbs green, and red is observed; but when the magnetic field is set up, blue-green light is seen at the analyser; for there are now two different kinds of light being absorbed, one of higher and one of lower frequency than the normal, and what is observed is the complementary spectrum. Again, if a tube of sodium is warmed to a point far short of that which would cause it to emit visible rays, and the vapour is passed into the magnet gap, at the moment when the magnetic field is set up the D line becomes visible in the observing spectroscope, *i. e.*, the emission spectrum is obtained of a substance which is not actually emitting light.

Mr. **Blakesley** said that no doubt the analyser was used at the position of extinction for convenience merely. In other positions the eye would be overwhelmed with light.

Mr. **Albert Campbell** then read a paper on "*The Magnetic Fluxes in Meters and other Electrical Instruments.*"

He has recently undertaken the measurement of the magnetic fluxes and fields in certain instruments, to determine the order of magnitude of the flux density. In other cases the *total* flux is measured; and in the tests on meters the power lost in the various parts of the instruments is determined. For the measurement of B the ordinary ballistic-galvanometer method is employed, with an exploring-coil. But for alternating fluxes two special methods are adopted, in the first of which the exploring-coil is in series with a heating-coil associated with a thermopile; in the second, a telephone is connected in series with the search-coil and a potentiometer resistance strip. A constant current is sent through the strip from the main alternate-current circuit supplying the meter or other apparatus; the telephone and search-coil therefore form a shunt to that circuit at the strip. The search-coil is put into position in the field to be tested, and the strip is then adjusted to give silence in the telephone. All these methods are described in detail in the paper, and very important deductions are made, especially as regards the influence of the earth's field on instruments generally assumed to be independent of the earth's H. In a few cases diagrams are given of the fluxes in magnets, showing exactly what proportion of the total flux is effective at the gap.

Dr. S. P. **Thompson** suggested that, as the paper was of great significance to all who were interested in the design of electric meters and other measuring instruments involving a knowledge of magnetic fluxes and their variation, an opportunity should be given for a full discussion.

The **President** proposed votes of thanks, and adjourned the discussion of Mr. Campbell's paper to the next meeting, on Nov. 11th.

NOTICES OF BOOKS.

An Introduction to the Science and Practice of Qualitative Chemical Analysis, Inorganic. By Chapman Jones, F.I.C., F.C.S. London: Macmillan and Co., Ltd.

This volume is one more addition to the already long list of text-books for Science students, and is the outcome of the author's experience as a demonstrator and examiner in Chemistry: it will doubtless be of great assistance to students attending Science classes. The methods of analysis are clearly stated, and great pains have been taken to give precise direction in every detail.

The object of the author has been to thoroughly ground the student in sound method in his work; but we are unable to avoid the impression that there is a danger of his trusting to his text-book rather than to his memory.

An original feature is the printing of the included tables of Analysis upon parchmentised paper, "so that if anything is spilled on the book as it lies open at any of the tables the result will not be so disastrous as it otherwise might be." This appears an unfortunate way of meeting a well-known difficulty with the average student, and seems to suggest working with a test-tube in one hand and the text-book in the other, a system to be deprecated.

In the table of atomic weights two values are given, one said to be deduced from the most reliable experimental data available (praseo- and neo-dymium are not included), and the second "sufficiently near for all the calculations for which the student may require atomic weights: thus the atomic weight of chlorine is given in the first column as 35·453, and in the second as 35·5. Surely it would have been better to have credited the student with a certain amount of reasoning power, and have left him to deduce this for himself.

A Pocket Dictionary of Hygiene. By C. T. Kingzett, F.I.C., and D. Homfray, B.Sc. London: Baillière, Tindall, & Cox, 20 & 21, King William Street, Strand.

An exceedingly useful little book, full of commonplace, but valuable, information. Although professedly the chief object of the authors has been to produce a concise dictionary for the use of medical and sanitary officers, it would undoubtedly prove of great service not only to those professionally interested in hygiene, but also to any one having household responsibilities.

The brief tables on the effects of vaccination would be a good lesson to the so-called "conscientious objector," could he be persuaded to read anything so matter-of-fact.

We must say we were surprised on finding an article on Röntgen rays, embracing Crookes's, Hertz's, and Röntgen's researches; but hygiene is a very inclusive subject.

The book is very well printed and conveniently arranged in alphabetical order, and not too large to be easily carried in the pocket.

The Cyanide Process for the Extraction of Gold, and its Application on the Witwatersrand Goldfields and Elsewhere. By M. Eissler. Second Edition, Enlarged. London: Crosby Lockwood and Son, 7, Stationers' Hall Court, Ludgate Hill.

The second edition of this valuable work will be welcomed by all interested in gold extraction; its thoroughly practical character renders it of the greatest value to metallurgists, especially those actively engaged in gold recovery

Mr. Eissler has spared no pains in his exposition of the process; it is clearly written, and there are plenty of illustrations as well as some fifteen folding plates giving detailed plans of the plants erected in various localities.

A good description is included of the Siemens-Halske process for the precipitation of gold from cyanide solutions, and an Appendix giving an up-to-date account of the cyanide plant recently erected at Golden Gate Mill, at the De la Mar Company, at Merceer, Utah, U.S.A.

A Short Manual of Analytical Chemistry, Qualitative and Quantitative, Inorganic and Organic, following the Course of Instruction given in the Laboratories of the South London School of Pharmacy. By John Muter, Ph.D., F.R.S.E., F.I.C., F.C.S. Eighth Edition, Illustrated. London: Simpkin, Marshall, Hamilton, Kent, and Co., Ltd.

The fact that this work has reached its eighth edition speaks eloquently as to its general appreciation, and the author is to be congratulated upon his success, due undoubtedly to the thoroughly practical manner in which the subject is handled: certainly it is not a "mere examination book," and the pharmaceutical student who makes good use of it cannot fail to acquire a solid grounding in the science. There are plenty of illustrations, particularly in the chapters upon manipulation, which are of very great value to the beginner, as they show, far more clearly than the most elaborate description, the proper way to conduct simple operations.

From a pharmaceutical point of view, the fact that this edition contains the present legal standards for drugs as fixed by the B.P. makes it valuable as a book of reference. It is well and clearly printed, and the price is so low as to place it within the reach of all.

Inorganic Chemistry, according to the Periodic Law. By F. P. Venable and Jas. Lewis Howe. Easton, Pennsylvania: The Chemical Publishing Co. 1898. Pp. vi.—266. 8vo. Illustrated.

"The Periodic Law has come to be the great central fact of chemistry; it has thrown new light upon the study of the science and is the very best aid to that study." This statement, enunciated in the Preface, forms the underlying principle throughout this book, thus securing thorough systematic instruction with economy of time. Scattered through the work are directions for simple experiments that have been found by experience well calculated to impress the subject upon the student. One hour of laboratory work is recommended in connection with each lecture. In Part I. the great principles of the science are laid down in an excellently clear style, developing especially the Periodic Law. The authors anticipate, however, the difficulties students encounter in attempting to comprehend the theories of chemistry, and therefore a good deal of the matter is repeated in suitable places when facts have been acquired which render explanations possible. At the same time it is scarcely practicable to start upon the study of the science without some such framework for the building.

The important facts of elementary chemistry are given with conciseness and clearness, the order in Part II. being H, Fl, Br, I, followed by O, S, Se, Te, N (atmosphere), P, As, Sb, and Bi. The space given to the several elements is proportioned to their relative importance with great nicety, and much economy of space is gained by treating together groups of analogous compounds.

After dealing with the elements, the authors introduce the student to hydrides, halides, oxides and sulphides, and other binary compounds. This arrangement is strictly logical, but it has the disadvantage of postponing the student's full acquaintance with such common substances as nitric and sulphuric acid until towards the close of the volume, although he has been using these acids in experimental work from the beginning.

The spelling recommended by the American Association for the Advancement of Science has been adopted only in part, the authors not venturing to write "sulfur" for the customary "sulphur," which was never justified etymologically.

Professor F. B. Venable, Ph.D., of the University of North Carolina, is well known as the author of "The Development of the Periodic Law" (1896), "A Short History of Chemistry" (1894), and many original investigations. Professor Jas. Lewis Howe, M.D., Ph.D., has recently published, through the Smithsonian Institution, an invaluable Bibliography of Platinum and associated metals. These two chemists have produced a book of great merit, being fully up to date (even krypton, neon, and metargon are briefly noticed), and well adapted for instruction.

The volume is well printed, but the paper seems unnecessarily bulky. There is an index. The buckram binding is serviceable. H. C. B.

MEETINGS FOR THE WEEK.

Monday, 7th.—Royal Institution, 5. General Monthly Meeting.
Friday, 11th.—Physical, 5. Discussion on Mr. Campbell's Paper on "The Magnetic Fluxes in Meters and other Electrical Instruments," to be opened by Prof. W. E. Ayrton, F.R.S. "Propagation of Damped Electrical Oscillations along Parallel Wires," by Prof. W. B. Morton, M.A. "Properties of Liquid Mixtures," by R. A. Lehfeldt.

THE CHEMICAL NEWS.

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THE CHEMISTRY OF THE STARS.*

By Sir J. NORMAN LOCKYER, K.C.B., F.R.S.

The importance of practical work, the educational value of the seeking after truth by experiment and observation on the part of even young students, are now generally recognised. That battle has been fought and won. But there is a tendency in the official direction of seats of learning to consider what is known to be useful, because it is used, in the first place. The fact that the unknown—that is, the unstudied—is the mine from which all scientific knowledge with its million applications has been won is too often forgotten.

Bacon, who was the first to point out the importance of experiment in the physical sciences, and who predicted the applications to which I have referred, warns us that "lucifera experimenta non fructifera quaerenda"; and surely we should highly prize those results which enlarge the domain of human thought and help us to understand the mechanism of the wonderful universe in which our lot is cast, as well as those which add to the comfort and the convenience of our lives.

It would be also easy to show by many instances how researches, considered ideally useless at the time they were made, have been the origin of the most tremendous applications. One instance suffices, Faraday's trifling with wires and magnets has already landed us in one of the greatest revolutions which civilisation has witnessed; and where the triumphs of electrical science will stop no man can say.

Fraünhofer at the beginning of this century examined sunlight and starlight through a prism. He found that the light received from the sun differed from that of the stars. So useless did his work appear that we had to wait for half a century till any considerable advance was made. It was found at last that the strange "lines" seen and named by Fraünhofer were precious indications of the chemical substances present in worlds immeasurably remote. We had, after half a century's neglect, the foundation of solar and stellar chemistry, an advance in knowledge equalling any other in its importance.

The first important matter which lies on the surface of such a general inquiry as this is that if we deal with the chemical elements as judged by the lines in their spectra, we know of the existence of oxygen, of nitrogen, of argon, representing one class of gases, in no celestial body whatever; whereas, representing other gases, we have a tremendous demonstration of the existence of hydrogen and helium.

We see, then, that the celestial sorting out of gases is quite different from the terrestrial one.

Among the non-metals there is a considerable development of carbon in some stars, and an indication of silicium in others, while among the metals are found chiefly Ca, Sr, Fe, Mg.

These elements do not exist indiscriminately in all celestial bodies.

From a spectroscopic study of those stars which resemble our sun, we learn that the atmospheres of some consist chiefly of those elements known to us as gaseous, of others chiefly metallic, and of others, again, carbon or compounds of carbon. This is evidence of variation in the chemical constitution of stellar atmospheres; also, as one of Kirchhoff's laws shows, that the hotter a mass of matter is, the further its spectrum extends into the ultra-violet. Hence, the hotter a star is, the further its complete or continuous spectrum will extend towards the ultra-violet.

Now to deal with three of the main groups of stars, we find the following very general result:—

Gaseous stars	Longest spectrum.
Metallic stars	Medium spectrum.
Carbon stars	Shortest spectrum.

Therefore—

Gaseous stars	Highest temperature.
Metallic stars	Medium temperature.
Carbon stars	Lowest temperature.

Hence the differences in apparent chemical constitutions are associated with differences of temperature.

Research also shows that, in the case of Mg, Fe, Ca, &c., by increasing the temperature in which they are volatilised, new lines are added or old ones intensified; applying this to stellar spectroscopy, it is found that—

Gaseous stars	..Highest temperature	Strong helium and faint enhanced lines.
Metallic stars	..Medium temperature	Feeble helium and strong enhanced lines. No helium and strong arc lines.
Carbon stars	..Lowest temperature	Faint arc lines.

It is clear now, not only that the spectral changes in stars are associated with, or produced by, changes of temperature, but that the study of the enhanced spark and the arc lines lands us in the possibility of a rigorous stellar thermometry, such lines being more easy to observe than the relative lengths of spectrum.

Many years of very detailed inquiry have convinced me that all stars save the hottest must be sorted out into two series—those getting hotter, and those, like our sun, getting cooler—and that the hottest stage in the history of a star is reached near the middle of its life.

The method of inquiry adopted has been to compare large-scale photographs of the spectra of the different stars, taken by my assistants at South Kensington; the complete harmony of the results obtained along various lines of other work carries conviction with it.

We find ourselves, then, in the presence of minute details exhibiting the workings of a chemical law, associated distinctly with temperature.

What, then, is the chemical law? It is this. In the very hottest stars we deal with the gases hydrogen, helium, and doubtless others still unknown, almost exclusively. At the next lowest temperatures we find these gases being replaced by metals in the state in which they are observed in our laboratories when the most powerful jar-spark is employed. At a lower temperature still, the gases almost disappear entirely, and the metals exist in the state produced by the electric arc. Certain typical stars showing these chemical changes may be arranged as follows:—

Stars getting hotter.	Hottest stars.	Stars cooling.
	Bellatrix	
ζ Tauri		β Persei
Rigel		γ Lyra
α Cygni		Castor
γ Cygni		Procyon
α Orionis		Arcturus and Sun

We get a great diversity, and we know that this diversity accompanies changes of temperature. We have also found that the sun, which we independently know to be a cooling star, and Arcturus, are identical chemically.

The next point we have to consider is whether the

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* Abstract of the Presidential Address to the Birmingham and Midland Institute, October 26, 1898.

absorption which the spectrum indicates for us takes place from top to bottom of the atmosphere, or only in certain levels.

In many of these stars the atmosphere may be millions of miles high. In each the chemical substances in the hottest and coldest portions *may* be vastly different; the region, therefore, in which this absorption takes place, which spectroscopically enables us to discriminate star from star, must be accurately known before we can obtain the greatest amount of information from our inquiries.

Our next duty then clearly is to study the sun—a star so near us that we can examine the *different parts* of its atmosphere, which we cannot do in the case of the more distant stars. By doing this we may secure facts which will enable us to ascertain in what parts of the atmosphere the absorption took place which produces the various phenomena on which the chemical classification has been based.

It is obvious that the general spectrum of the sun, like that of stars generally, is built up of all the absorptions *which can make themselves felt* in every layer of its atmosphere from bottom to top, that is from the photosphere to the outermost part of the corona. Let me remind you that this spectrum is *changeless* from year to year.

Now sun-spots are disturbances produced in the photosphere; and the chromosphere, with its disturbances, called prominences, lies directly above it. Here, then, we are dealing with the lowest part of the sun's atmosphere. We find first of all that in opposition to the changeless general spectrum, great changes occur with the sun-spot period, both in the spots and chromosphere.

The spot spectrum is indicated, as was found in 1866, by the widening of certain lines; the chromospheric spectrum, as was found in 1868, by the appearance at the sun's limb of certain bright lines. In both cases the lines affected seen at any one time are relatively few in number.

In the spot spectrum, at a sun-spot minimum, we find iron lines chiefly affected; at a maximum they are chiefly of unknown or unfamiliar origin. At the present moment the affected lines are those recorded in the spectra of vanadium and scandium, with others never seen in a laboratory. That we are here far away from terrestrial chemical conditions is evidenced by the fact that there is not a gramme of scandium available for laboratory use in the world at the present time.

Then we have the spectrum of the prominences and the chromosphere. That spectrum we are enabled to observe every day when the sun shines, as conveniently as we can observe that of sun-spots. The chromosphere is full of marvels. At first, when our knowledge of spectra was very much more restricted than now, almost all the lines observed were unknown. In 1868 I saw a line in the yellow which I found behaved very much like hydrogen, though I could prove that it was not due to hydrogen; for laboratory use the substance which gave rise to it I called helium. Next year I saw a line in the green at 1474 of Kirchhoff's scale. That was an unknown line, but in some subsequent researches I traced it to iron. From that day to this we have observed a large number of lines. They have gradually been dragged out from the region of the unknown, and many are now recognised as enhanced lines, to which I have already called attention as appearing in the spectra of metals at a very high temperature. The best time for observation is undoubtedly during an eclipse.

A tremendous flood of light has been thrown upon it by the use of large instruments constructed on a plan devised by Respighi and myself in 1871. These give us an image of the chromosphere painted in each one of its radiations, so that the exact locus of each chemical layer is revealed. One of the instruments employed during the Indian eclipse of this year is that used in photographing the spectra of stars, so that it is now easy to place photographs of the spectra of the chromosphere obtained during a total eclipse and of the various stars side by side.

Studying the spectra photographed during the eclipse of this year we see that practically the lower part of the sun's atmosphere, if present by itself, would give us the lines which specialise the spectra of γ Cygni or Procyon.

I recognise in this result a veritable Rosetta stone which will enable us to read the celestial hieroglyphics presented to us in stellar spectra, and help us to study the spectra and to get at results much more distinctly and certainly than ever before.

One of the most important conclusions we draw from the Indian eclipse is that, *for some reason or other*, the lowest hottest part of the sun's atmosphere does not write its record among the lines which build up the general spectrum so effectively as does a higher one.

There was another point especially important on which we hoped for information, and that was this:—Up to the employment of the prismatic camera insufficient attention had been directed to the fact that in observations made by an ordinary spectroscope, no true measure of the height to which the vapours or gases extended above the sun could be obtained; early observations, in fact, showed the existence of glare between the observer and the dark moon; hence it must exist between us and the sun's surroundings.

The prismatic camera gets rid of the effects of this glare, and its results indicate that the effective absorbing layer—that, namely, which gives rise to the Fraünhofer lines—is much more restricted in thickness than was to be gathered from the early observations.

It happened that I was the only person that saw both the eclipse of 1871 at the maximum of the sun-spot period and that of 1878 at minimum: the corona of 1871 was as distinct from the corona of 1878 as anything could be. In 1871 we got nothing but bright lines indicating the presence of gases, namely, hydrogen and another, since provisionally called coronium. In 1878 we got no bright lines at all, so I stated that probably the changes in the chemistry and appearance of the corona would be found to be dependent upon the sun-spot period, and recent work has borne out that suggestion.

General Results regarding the Locus of Absorption in Stellar Atmospheres.

We learn from the sun, then, that the absorption which defines the spectrum of a star is the absorption of a middle region, one shielded both from the highest temperature of the lowest reaches of the atmosphere where most tremendous changes are continually going on, and the external region where the temperature must be low, and where the metallic vapours must condense.

So far I have only dealt in detail with the hotter stars, but I have pointed out that we have two distinct kinds of coolest ones, the evidence of their much lower temperature being the shortness of their spectra. In one of these groups we deal with absorption alone, as in those already considered; we find an important break in the phenomena observed; helium, hydrogen, and metals have practically disappeared, and we deal with carbon absorption alone.

But the other group of coolest stars presents us with quite new phenomena. We no longer deal with absorption alone, but accompanying it we have radiation, so that the spectra contain both dark lines and bright ones. Now since such spectra are visible in the case of new stars, the ephemera of the skies, which may be said to exist only for an instant relatively, and when the disturbance which gives rise to their sudden appearance has ceased, we find their places occupied by nebulæ, we cannot be dealing here with stars like the sun, which has already taken some millions of years to slowly cool, and requires more millions to complete the process into invisibility.

The bright lines seen in the large number of permanent stars which resemble these fleeting ones—*new stars*, as they are called—are those discerned in the once mysterious nebulæ which, so far from being stars, were supposed not many years ago to represent a special order of created things.

Now the nebulæ differ from stars generally in the fact that in their spectra we have practically to deal with radiation alone; we study them by their bright lines, the conditions which produce the absorption by which we study the chemistry of the hottest stars are absent.

A New View of Nebulæ.

Passing over the old views, among them one that the nebulæ were holes in something dark which enabled us to see something bright beyond, and another that they were composed of a fiery fluid, I may say that not long ago they were supposed to be masses of gases only, existing at a very high temperature.

Now, since gases may glow at a low temperature as well as at a high one, the temperature evidence must depend upon the presence of cool metallic lines and the absence of the enhanced ones.

The nebulæ, then, are relatively cool collections of some of the permanent gases and of some cool metallic vapours, and both gases and metals are precisely those I have referred to as writing their records most visibly in stellar atmospheres.

Now can we get more information concerning this association of certain gases and metals? In laboratory work it is abundantly recognised that all meteorites (and many minerals) when slightly heated give out permanent gases, and under certain conditions the spectrum of the nebulæ may in this way be closely approximated to. I have not time to labour this point, but I may say that a discussion of all the available observations to my mind demonstrates the truth of the suggestion, made many years ago by Prof. Tait before any spectroscopic facts were available, that the nebulæ are masses of meteorites rendered hot by collisions.

Surely human knowledge is all the richer for this indication of the connection between the nebulæ, hitherto the most mysterious bodies in the skies, and the "stones that fall from heaven."

Celestial Evolution.

But this is, after all, only a stepping-stone, important though it be. It leads us to a vast generalisation. If the nebulæ are thus composed, they are bound to condense to centres however vast their initial proportions, however irregular the first distribution of the cosmic clouds which compose them; each pair of meteorites in collision puts us in mental possession of what the final stage must be. We begin with a feeble absorption of metallic vapours round each meteorite in collision; the space between the meteorites is filled with the permanent gases driven out further afield and having no power to condense. Hence dark metallic and bright gas lines. As time goes on the former must predominate, for the whole swarm of meteorites will then form a gaseous sphere with a strongly heated centre, the light of which will be absorbed by the exterior vapour.

The temperature-order of the group of stars with bright lines as well as dark ones in their spectra, has been traced, and typical stars indicating the chemical changes have been as carefully studied as those in which absorption phenomena are visible alone, so that now there are no breaks in the line connecting the nebulæ with the stars on the verge of extinction.

Here we are brought to another tremendous outcome, that of the evolution of all cosmical bodies from meteorites, the various stages recorded by the spectra being brought about by the various conditions which follow from the conditions.

These are, shortly, that at first collisions produce luminosity among the colliding particles of the swarm, and the permanent gases are given off and fill the interspaces. As condensation goes on, the temperature at the centre of condensation always increasing, all the meteorites in time are driven into a state of gas. The meteoritic bombardment practically now ceases for lack of material, and the future history of the mass of gas is that of a cooling body, the violent motions in the atmosphere while condensation was going on now being replaced by a relative calm.

The absorption phenomena in stellar spectra are not identical at the same mean temperature on the ascending and descending sides of the curve, on account of the tremendous difference in the physical conditions.

In a condensing swarm, the centre of which is undergoing meteoritic bombardment from all sides, there cannot be the equivalent of the solar chromosphere; the whole mass is made up of heterogeneous vapour at different temperatures, and moving with different velocities in different regions.

In a condensed swarm, of which we can take the sun as a type, all action produced from without has practically ceased; we get relatively a quiet atmosphere and an orderly assortment of the vapours from top to bottom, disturbed only by the fall of condensed metallic vapours. But still, on the view that the differences in the spectra of the heavenly bodies chiefly represent differences in degree of condensation and temperature, there can be, *au fond*, no great chemical difference between bodies of increasing and bodies of decreasing temperature. Hence we find, at equal mean temperatures on opposite sides of the temperature curve, this chemical similarity of the absorbing vapours proved by many points of resemblance in the spectra, especially the identical behaviour of the enhanced metallic and cleveite lines.

A quarter of a century ago I pointed out that all the facts then available suggested the hypothesis that in the atmospheres of the sun and stars various degrees of "celestial dissociation" were at work, a "dissociation" which prevented the coming together of the finest particles of matter which at the temperature of the earth, and at all artificial temperatures yet attained here, compose the metals, the metalloids, and compounds.

On this hypothesis the so-called atoms of the chemist represent not the origins of things, but only early stages of the evolutionary process.

At the present time we have tens of thousands of facts which were not available twenty-five years ago. All these go to the support of the hypothesis, and among them I must indicate the results obtained at the last eclipse, dealing with the atmosphere of the sun in relation to that of the various stars of higher temperature to which I called your attention. In this way we can easily explain the enhanced lines of iron existing practically alone in Alpha Cygni. I have yet to learn any other explanation.

AMORPHOUS SILICA.

By ROBERT MELDRUM, F.C.S.

This investigation was originally carried out with the view of making a complete chemical and physical exexamination of amorphous silica, but after being in progress for some time it had to be abandoned through the pressure of other work. The following is a record of the results so far obtained:—

A sample of SiO_2 was prepared by adding 200 c.c. strong HCl to 200 c.c. of commercial sodium silicate, of sp. gr. 1·526, containing 12·87 per cent Na_2O and 31·98 per cent SiO_2. The mass was constantly stirred for thirty minutes, so as to allow the acid to thoroughly penetrate the thick gelatinous mixture, the yellow liquid decanted. and the SiO_2 washed repeatedly with boiling water until free from chlorine. After drying slowly in the air for a week, the resulting product was a snow-white, granular, coarse powder, very porous and light. Three determinations of the loss on ignition, at red heat, gave 30·4, 30·5, 30·35—average 30·41 per cent. After drying over sulphuric acid, until weight remained constant, lost 22·90 per cent, = 9·74 per cent H_2O in desiccated SiO_2. The specific gravity of the anhydrous silica was found to be 1·990, 2·0964; of the air-dry, 2·0543. Loss of air-dry at 100° C. = 24·75 per cent = 7·52 per cent H_2O in residue. When strongly ignited for thirty minutes over blowpipe, digested in water for twenty-four hours, allowed to dry in air until weight remained constant, absorbed parts per 100, 4·05, 4·65. Another portion of the strongly ignited sample, exposed to a moist atmosphere, absorbed 6·85 parts per 100.

Another sample was prepared, exactly as described above, but using a weaker solution of silicate, and dilute acid (equal parts strong HCl and water). Sp. gr. of air-dry 1·709, 1·7346. Its shrinkage was ascertained by filling a very strong-stoppered bottle of 8 c.c. capacity, and beating the bottom with a small mallet, adding more material and repeating this until the level ceased to diminish, the SiO_2 being previously passed through a 40-sieve. The bottle held 5·01, 5·08, and 5·00 grms.; thus showing that measuring powders by this method is fairly accurate. After ignition these were found to occupy volumes of 5·2 cc., 5·5 c.c., and 5·0 c.c., equal to 65, 68, and 62·5 per cent of original volume. The shrinkage is, therefore, much greater than the loss by weight on ignition, the latter being 25·80 per cent. Loss at 100° C. = 19·15, 19·35 per cent = 8·11 per cent H_2O in residue.

The following experiment was made to ascertain to what extent the density of SiO_2 would be increased when liberated from a strong solution of silicate, and in the presence of as little water as possible. For this purpose strong H_2SO_4 was poured very gradually into the silicate, well agitating and mixing the mass, so as to allow thorough decomposition. It was then allowed to digest for an hour, water added, and the amorphous silica partially washed by decantation, boiled with dilute HCl, and repeatedly boiled with distilled water till free from chloride. The variety obtained by this process is more granular, hard, and brittle, but less opaque, than the others. After strong ignition at red heat its specific gravity was found to be 2·008, 2·006. Lost over H_2SO_4, 23·55 per cent = 9·83 per cent H_2O in residue. Loss at red heat, 23·55 per cent. No increase of temperature was observed on moistening the anhydrous SiO_2 with water.

Of the various degrees of hydration obtained as noted above, the only ones approaching a definite hydrate are those resulting from the dehydration of the air-dry silica over H_2SO_4, which agree closely with the formula $3SiO_2.H_2O$. This confirms Merz's observation that the same hydrate is formed by prolonged drying of precipitated SiO_2 over H_2SO_4.

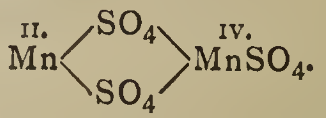
Note.—The samples were washed until free from gelatinous silica.

THE
FORMATION OF ALUMS BY ELECTROLYSIS.*

By JAS. LEWIS HOWE and E. A. O'NEAL.

The work herein described had for its special end the formation of alums of manganese; and while, in this particular, success was not attained, it is felt that it is well to place the work on record, especially as phases of it are capable of further development, from which interesting results may be hoped.

Manganese salts in which the metal is trivalent, are not very satisfactorily known. Potassium and ammonium manganic alums have been described by Mitscherlich, but to manganic sulphate, $Mn_2(SO_4)_3$, Franke (*Journ. Prakt. Chem.*, [2], xxxvi., 451), who has most thoroughly studied it, gives the formula—



$$\overset{\text{II.}}{\mathrm{Mn}}\begin{matrix}\diagup SO_4\diagdown\\ \diagdown SO_4\diagup\end{matrix}\overset{\text{IV.}}{\mathrm{Mn}}SO_4.$$

A salt of this constitution could hardly give an alum, and the literature of the manganese alums is very unsatisfactory. It was hoped by using the oxidising action of the electric current on a solution of manganous sulphate in the presence of an alkaline sulphate, manganic alum might crystallise out, and the reaction was studied with other metals for the sake of familiarity with the method and for comparison. Incidentally several alums were obtained and analysed which have not been previously described.

a. Iron Alums.—Apparatus:—Positive electrode, a platinum dish of about 250 c.c. capacity resting on a coil of heavy copper wire; negative electrode, a coil of heavy platinum wire; diaphragm, the lower portion of the porous cup of a Bunsen cell. In different experiments different batteries were used, but Bunsen or crowfoot cells were generally used.

The following is a specimen experiment:—Inner solution, ferrous sulphate strongly acidified with sulphuric acid; outer solution, saturated with ferrous sulphate and ammonium sulphate, and also strongly acidified with sulphuric acid; six crowfoot cells; current, 0·04 ampère. In forty-eight hours a large crop of beautiful iron-ammonium alum crystals, of perfect octahedral form, were produced. In one experiment, with solutions as above and apparatus also, except that Bunsen cells were used, with current 0·02 ampères, 41 grms. of iron-ammonium alum were obtained in twenty-four hours. This method is probably applicable to the formation of this alum on a commercial scale, having as its advantages the ease with which it is conducted and the fine quality of the product. Owing to the lesser solubility of potassium sulphate, the method, while successful, does not give such good results in the formation of iron-potassium alum.

The formation of iron-sodium alum was tried, using solutions as above, with sodium sulphate substituted for ammonium sulphate. Current, four Bunsen cells. After twelve hours the outer solution (+) was pink, and in twenty-four hours had become dark purple, resembling almost a solution of potassium permanganate, while oxygen bubbles were given off at the positive pole. A little ferrous sulphate solution was added, at which the colour at once disappeared, but after several hours with the current, it again became dark purple. The colour disappeared at once with reducing agents. The colour was that of ferrates, but the presence of ferric acid is hardly probable, and the solution being strongly acid, ferrates could not be present. It seems more probable that the compound was one of persulphuric acid. No crystals could be obtained even by using a freezing mixture. Some of the solution set aside for several weeks left, on evaporation, a hard, dirty violet, crystalline mass, containing crystals somewhat triangular in form, which were very insoluble in both water and hydrochloric acid. This substance was not pure and was not further investigated.

Iron-rubidium Alum and Iron-cæsium Alum, $RbFe(SO_4)_2.12H_2O$ *and* $CsFe(SO_4)_2.12H_2O$.—As no description of these alums was found in chemical literature, they were both formed and analysed. In working with rubidium and cæsium salts, a smaller form of apparatus was used, the positive pole being a platinum crucible of 11 c.c. capacity, the negative pole a coil of heavy platinum wire, and the diaphragm an unglazed porcelain annealing cup. The cup was filled as above with a solution of ferrous sulphate, and the platinum crucible, which rested in a ring of heavy copper wire, with a solution of ferrous sulphate and rubidium sulphate or cæsium sulphate. Both solutions were strongly acid with sulphuric acid. Very considerable crops of both the rubidium and cæsium alums were obtained in the form of small octa-

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* Read at the Boston meeting of the American Chemical Society, August, 1898. From the *Journal of the American Chemical Society*, vol. xx., No. 10.

hedra. They are of a delicate violet colour, turning slightly greenish on exposure to the air. They resemble potassium-alum in every respect, except that the rubidium alum is very slightly soluble and the cæsium alum almost insoluble in water.

Analysis.

	Calculated for $RbFe(SO_4)_2.12H_2O$.	Found. I.	Found. II.
H_2O	39·3	39·1	38·9
SO_4	34·9	35·2	—
Fe	10·2	11·0	—

	Calculated for $CsFe(SO_4)_2.12H_2O$.	Found. I.	Found. II.
H_2O	36·2	36·1	36·3
SO_4	32·2	33·3	—
Fe	9·4	10·4	—

b. Cobalt Alums.—The cobalt, potassium, and ammonium alums were discovered by Marshall (*Proc. Roy. Soc. Edin.*, xiv., p. 203; *J. Chem. Soc.*, lix., p. 760), whose work was the incentive to that described in this paper. The rubidium and cæsium alums were made by us and have not been hitherto described. The apparatus used was the smaller form, as for the iron rubidium alum, and the experiments conducted similarly. The outer (positive) solution was kept quite strongly acid with concentrated sulphuric acid. Four Bunsen cells were used; current 0·16 to 0·19 ampère. At first it was found that in some experiments beautiful crystals were obtained in considerable quantity, in others no crystals at all. This was soon found to be due to the temperature. On nights when the laboratory was cool the crystals formed readily. By keeping the crucible with its support immersed in a beaker of water, ill effects from heating by the current were avoided and the alums readily obtained.

It is thus seen that the rubidium and cæsium alums are much more readily formed than the potassium and ammonium, as would be expected. These alums are minute, deep blue octahedra, stable in dry air, but gradually decomposing in moist air with formation of cobalt sulphate; the cæsium alum showed occasional cube faces. In water the alums are quickly decomposed with evolution of oxygen and reduction to cobalt sulphate. In dilute hydrochloric acid and in dilute sulphuric acid the crystals dissolve to a blue solution. In concentrated hydrochloric acid and concentrated sulphuric acid they are decomposed, giving in the latter case a brown solution.

Several methods of analysis were tried. On heating to 200° the salt becomes whitish pink, and apparently contains free sulphuric acid from its decomposition into cobalt sulphate, more or less water being thus retained. The best method of analysis was found to be the following:—The salt is mixed with anhydrous sodium carbonate in a platinum boat, and heated in a combustion tube in an oxygen stream. The water is absorbed in a calcium chloride tube. The residue is treated with hot water. The filtrate contains the Cs (or Rb) and the SO_4, which are estimated as cæsium chloroplatinate and barium sulphate. The insoluble residue, cobalt oxide, is heated in a hydrogen stream and weighed as metallic cobalt.

	Calculated for $RbCo(SO_4)_2.12H_2O$.	Found. I.	Found. II.
Rb	15·5	15·9	—
Co	10·7	11·9*	—
SO_4	34·8	35·4	—
H_2O	39·1	37·9	38·2†

	Calculated for $CsCo(SO_4)_2.12H_2O$.	Found.‡
Cs	22·1	22·5
Co	9·8	10·2
SO_4	32·0	32·2
H_2O	36·0	36·7

* As $CoSO_4$ after removal of Rb as Rb_2PtCl_6.
† By loss at 200°.
‡ By method described above.

c. Chromium Alums.—An experiment was tried using a solution of potassium chromate strongly acidified with sulphuric acid as electrolyte for the negative pole, and dilute sulphuric acid for the positive. After thirty-six hours no chrome alum was obtained, but considerable potassium sulphate was deposited, strongly coloured green by the chromic solution present. On substituting ammonium chromate for the potassium chromate a considerable crop of chromium ammonium alum crystals was obtained at the negative pole. These crystals were very small. Four Bunsen cells were used in these experiments. This method of electrical reduction has been used by Piccini for the formation of vanadium (*Gazz. Chim. Ital.*, xxv., [2], 451) and titanium (*Ibid.*, xxv. [2], 542) alums.

d. Experiments with Manganese.—These experiments were carried out in both the large and small apparatus; with manganese sulphate and ammonium, rubidium, and cæsium sulphates; with varying quantities of free sulphuric acid in the electrolytes; with different strengths of current; and at various temperatures. The solution at the positive pole in every case became deep wine colour, and the higher oxide of manganese was deposited. In one case only were a few minute octahedral crystals found in a rubidium manganese solution. These were deep wine colour, and qualitatively contained manganese. It is not, however, improbable that these were crystals of common alum coloured by manganese. In an experiment with ruthenium such crystals were obtained, the aluminum being probably derived from the porcelain diaphragm. In a number of cases the black precipitate at the positive pole, supposed to be manganese dioxide, when allowed to stand with concentrated sulphuric acid, showed itself under the microscope to be made up of flat, transparent, pale, wine-coloured crystals, resembling elongated hexagonal plates. These are not readily soluble in water or acids. They were not further investigated.

The electrolytical method does not seem to be applicable to the formation of manganese alums from manganous salts.* It is hoped later to try the electrolytic reduction of manganates and permanganates.

e. Experiments with Ruthenium.—No crystallised oxysalts of ruthenium are known. As the double salts of the trichloride crystallise well, an effort was made to obtain an alum by the electrolytic reduction of the nitrosochloride. The small apparatus was used. The solution at the negative pole was a solution of cæsium ruthenium nitrosochloride, $Cs_2\overset{IV}{Ru}Cl_5NO$, which had been boiled some time with sulphuric acid, and which might be supposed to contain the nitrososulphate. It was hoped to reduce the nitroso group and split it off as ammonia, leaving trivalent ruthenium in the presence of sulphuric acid and cæsium sulphate, the most favourable condition for alum formation. No sign of alum was found, nor did the electrolysed solution show reaction for trivalent ruthenium. A considerable quantity of ruthenium tetroxide, RuO_4, was given off. This was probably owing to oxidation at the positive pole, some of the ruthenium solution having penetrated the diaphragm into the sulphuric acid which surrounded the positive pole. The formation of ruthenium tetroxide by electrolytic oxidation has not been previously noticed. Further experiments with other ruthenium compounds are being carried on.

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* Since the above was in type, a further article by Piccini has appeared in the *Zeitschrift für Anorganische Chemie*, xvii., 361, describing the formation of the cæsium manganese alum by electrolytic oxidation, in a method apparently like that described in this paper. No particulars regarding current, &c., are given. This would seemingly settle the question of the trivalence of manganese in manganic salts. Attention is called, as in our paper, to the advantage in using rubidium and cæsium compounds where it is desired to obtain difficultly crystallisable compounds. Piccini's result renders it probable that the few octahedra obtained in our rubidium manganese experiment were really rubidium manganese alum; he also found his alum contaminated by aluminum from the diaphragm.

THE TRANSITION TEMPERATURE OF SODIC SULPHATE, A NEW FIXED POINT IN THERMOMETRY.*

By THEODORE WILLIAM RICHARDS.

(Concluded from p. 230).

Third Problem.—The Effect of Varying the Mass of the Phases.

THEORETICALLY, of course, a change in the relative amount of the phases should cause no difference in the nonvariance of the point under consideration provided that no one phase totally disappears. But since the superficial area of either solid present is a factor in determining the speed of the adjustment of the equilibrium, it was thought that varying proportions might cause a slightly varying "temperature lag." Nevertheless, as a matter of fact, no reasonable increase in the amount of either of the solids or of the liquid seemed to cause the least effect, provided that the process was one of melting and not of solidifying, and the mixture was properly stirred. The Beckmann thermometer remained always at 4·760 as long as the barometer stood near to the normal height. In order to insure the rapid establishment of the equilibrium it was our custom to have always some anhydrous powder present in the first place. This precaution also renders harmless drops of water introduced on the washed thermometer or the stirrer. It is well to powder also the hydrated salt, or at least to use it in the form of fine crystals, so as to increase its surface.

Since the point in question seems then to fulfil all the requirements of an accurate standard of reference, manifestly its relations to the international standard should be established.

II. *Reference to the International Standard.*

The only good thermometers indicating 33° at hand in the chemical laboratory are two of a set (one of which has already been mentioned) made by Baudin, and these have not been accurately calibrated. On one occasion thermometer Baudin No. 9389 indicated 32·570° as the point in question, and immediately afterward came to 0·097° in pure melting ice, a difference of 32·473°. Subsequently the same thermometer indicated a change of 32·560 − 0·086 = 32·474°; while the other thermometer (No. 9390) gave on two successive trials, separated by perhaps a week, 32·560 − 0·084 = 32·476°, and 32·550 − 0·083 = 32·467°. The mean of all these values is 32·472°, and to this about 0·009 (see tables by Rimbach in "Landolt und Börnstein," page 143) must be added to correct for the column of 10° exposed to the temperature of the room (about 26°). No other corrections are possible, and there is no further guarantee of the accuracy of the number 32·481° than the evident care used in the construction of the thermometers and the fact that they agree very closely. It is probable that the instruments were made to be used vertically, hence no correction to the horizontal position is needed.

In order to decide more definitely the exact value, Prof. Sabine was so kind as to bring from the Jefferson Physical Laboratory of Harvard University two of the admirable standards in use at that institution. These two instruments, the thermometers Nos. 11,142 and 11,143 of Tonnelot, have been subject to extremely minute scrunity and calibration. They are of course accompanied by a very detailed report from the Bureau Internationale des Poids et des Mesures, and upon this are based all the corrections recorded below, except the last. This one, necessitated by the fact that the thermometers were not wholly immersed in the constant mixture, was calculated from the relative cubic expansion of glass and mercury. The length of the column exposed to the temperature of the room (25·5°) was estimated carefully with the help of another thermometer, and was found to be about 22°, allowing for the conductivity of the glass and mercury. The correction, 0·024, agrees closely with Rimbach's (*loc. cit.*) empirical values, although his were not intended for such small corrections; probably it is not more than 0·003° in error.

Both thermometers are about 6 decimetres long, and have their hundred degrees divided into tenths. With the help of the accurate Geneva cathetometer employed, they could probably be read to within 1/500°. The readings were made with the co-operation of Prof. W. C. Sabine.

The Transition Temperature of Sodic Sulphate.

	Thermom. 11,142 Tonnelot.	Thermom. 11,143 Tonnelot.
Reading at transition point	+32·400	+32·498
Reading in meling ice	+ 0·120	+ 0·101
Uncorrected difference	+32·280	+32·397
Correction for calibration	+ 0·147	+ 0·028
" " interior press (32°)..	+ 0·0330	+ 0·0328
" " " " (0°) ..	− 0·0076	− 0·0075
" " exterior press (32°)	− 0·0006	− 0·0006
" " " " (0°)	+ 0·0007	+ 0·0007
" size of divisions	+ 0·0104	+ 0·0059
" for projecting column..	+ 0·024	+ 0·024
Transition point according to mean Parisian mercury thermometer..	+32·487	+ 32·480

The purest sodic sulphate, and ice from water which had just been twice distilled in platinum (from permanganate, and then from a trace of acid potassic sulphate) were used, and the usual precautions of all kinds were taken. The readings were made with the thermometers vertical: they are reduced to the horizontal position above. The corrected barometer stood at 761 m.m. during the higher readings, and at 762·5 when the thermometers were in ice. The middles of the bulbs were about 45 m.m. below the surface of the inverting mixture, and about 37 m.m. under the ice water. The pressures corresponding are about 4·5 m.m. and 5·7 m.m. of mercury respectively. The sum total of the corrections for exterior pressure is wholly insignificant; they are included above only for the sake of completeness. One division of No. 11,142 equals 1·000320 standard mercury degrees, while one of No. 11,143 equals 1·000181 degrees.

The two results (32·487° and 32·480°) are probably as nearly equal as could be expected, considering that three of the four readings unfortunately fell on dividing lines.

The agreement of the average 32·484 with the result 32·481, obtained from Baudin's uncorrected instruments, is notable; evidently the empirical graduation of the older day included a close approximation to most of the corrections. The result of Löwenherz, 32·39°, is the only previous value with which it is worth while to compare this, but his was meant only for relative work, and was referred merely to "a normal thermometer" of uncertain origin.

While it would be unsafe to predict the precise limit of error of the final value 32·484° (or 32·379 referred to the hydrogen thermometer) the result is certainly near enough to the truth to be a great boon to those who have not a standard instrument at their disposal. If, as is usually the case, it is only desired to attain a result accurate to within 1/100 degree, the thermostat is unnecessary. Surprisingly accurate results may be obtained in the ordinary Beckmann freezing-point apparatus, if the outer bath is a degree or two above the point desired (see *ante*). In fact, it is really an easier point to use than either of the old points, for one can keep neither ice nor steam always at hand in a bottle. Probably the inversion temperature might be of great use as a means of maintaining large vessels at a perfectly constant temperature;

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* From the *American Journal of Science*, vol. vi., 1898; also *Zeitschr. Phys. Chem.*, xxvi., 691.

this point deserves consideration. Moreover, while sodic sulphate has several advantages as a standard, there are undoubtedly many other substances which would also serve at other temperatures. One of these, calcic nitrate, inverting at about 42·7°, is at present under investigation at this laboratory, and it is hoped that a complete temperature-scale of standards may be established. It is also hoped that with an admirable new air-thermometer, at present nearly finished in the Jefferson Physical Laboratory, a direct determination of the transition temperature of sodic sulphate may be made in terms of the hydrogen standard.

In brief, this preliminary paper shows that sodic sulphate "melts" at almost exactly 32·48° according to the mean mercury thermometer, and that this temperature is so easily obtained and so constant as to be of great use in the future of thermometry and thermostatics.

THE COLORIMETRIC ESTIMATION OF SMALL AMOUNTS OF CHROMIUM,

WITH SPECIAL REFERENCE TO

THE ANALYSIS OF ROCKS AND ORES.*

By W. F. HILLEBRAND.

(Concluded from p. 228).

The Colorimetric Apparatus and its Use.

The glasses employed were of approximately square section, about 12 c.m. high and $3\frac{3}{10}$ c.m. inside measurement, with exactly parallel sides, and of course as nearly alike as they could be obtained. One pair of opposite sides of each should be blackened. With glasses of the thickness mentioned it is generally advisable to use from 5 to 10 c.c. of standard at a time, and to so regulate the strength of the solution to be tested that it shall contain more than 2 m.grms. chromic oxide in 100 c.c., which is about the limit of distinct visibility in a thickness of $3\frac{3}{10}$ c.m.

In order to exclude the effect of side light in this and other similar methods (titanium, for instance), it is very convenient to have a simple light box that can be easily held in one hand, about 35 c.m. long and 13 to 14 c.m. square, painted black inside and out and with one end closed by a piece of ground glass, the other open. For a space equal to the width of the glasses the cover is removed at the top next the glass end, to permit of the insertion of the glasses, side by side, in such a way that no light shall penetrate around their sides or between them. A stiffly-sliding black cardboard shutter is movable up and down immediately back of the glasses, so that all light can be cut off except that which comes through the liquid.

Precautions of this kind are necessary if accurate results are to be counted on. Except for mere traces, this simple combination of glasses and darkened box ensures greater accuracy and rapidity of work than Nessler tubes and is preferable likewise, so far as my own experience goes, to expensive instruments like the colorimeter of Soleil-Duboscq, &c. The glasses should, of course, have exactly parallel sides and equal diameters, though they may perhaps be made with advantage rather narrower in one direction to permit of using smaller bulks of liquid.

In making the colour comparisons, the box is best held close to a window, so as to get a full strong light. The condition of the light seems to make an appreciable difference in the accuracy of the comparisons, all of which were made by daylight.

Accuracy of Results.

Especially for comparatively and very small amounts of chromium the method gives exact results, better than can ordinarily be hoped for from any gravimetric method, considering the fact that, as a rule, other substances are present which it is extremely difficult to remove completely.

A few comparisons between colorimetric and gravimetric determinations of chromium in a few rocks are here given to show the order of agreement, the former having been made several months and even years after the latter.

Gravimetric. Per cent.	Colorimetric. Per cent.
Trace	0·018
0·05	0·051
0·14	0·12
0·08	0·083
Trace	0·013
None	0·0086
None	0·0067

The outcome was somewhat of a surprise, for it was scarcely to be expected that the long and laborious gravimetric separations should have resulted so well as they are shown to have done. It should be mentioned that, for the gravimetric tests, but one or two grms. at most were used, which accounts for the reported absence of chromium in two instances, this report being based on the lack of colour in the aqueous extract of the alkaline fusion after removal of manganese.

No experiments have been made with high percentages, but the tables give with certainty the degree of accuracy even then attainable. Whether the chromic oxide to be estimated is one-tenth per cent or 100 per cent, the percentage result is the same provided the dilution is alike in each case. For instance, if 99·5 per cent is found in a total solution of 100 c.c. containing 0·01 grm. chromic oxide, the same percentage holds if the total volume were ten litres holding 1 grm. chromic oxide.

It is probably inadvisable to increase the strength of the standard much above that of No 2 above, containing two-tenths m.grm. chromic oxide in form of potassium chromate to the cubic centimetre.

No tests have been made with other alkaline solutions than sodium carbonate, in order to ascertain if there is a difference in the colour intensities for like dilution, nor is it probably important to do so.

ON THE DETERMINATION OF MANGANESE AS THE PYROPHOSPHATE.*

By F. A. GOOCH and MARTHA AUSTEN.

For the estimation of manganese in a gravimetric way when accuracy is a consideration, recourse is usually taken to the excellent method of Prof. Wolcott Gibbs (*Am. Journ. Sci.*, xliv., 216). This method consists in the precipitation of a manganous salt by an alkaline phosphate, the conversion of the tribasic phosphate into the ammonium manganese phosphate, and the weighing of the product of ignition as the pyrophosphate.

By Dr. Gibbs's original method the orthophosphate of manganese was precipitated by hydrogen disodium phosphate in large excess above the quantity required to cause the precipitation. The flocky white precipitate was dissolved either in sulphuric or hydrochloric acid, and precipitated again at the boiling temperature by ammonia in excess. This semi-gelatinous precipitate on boiling or long standing even in the cold becomes crystalline, the crystals forming beautiful talcose scales which have a pearly lustre and a pale rose colour. The precipitate was filtered off, washed with hot water, dried, and ignited. The results obtained by Dr. Gibbs's students for the pyrophosphate accord closely with the theory.

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* Read before the Washington Section, March 10, 1898. From the *Journal of the American Chemical Society*, xx., No 6, June, 1898.

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, 1898, vol. vi., p. 233.

Fresenius (*Zeit. für Anal. Chem.*, vi., 415) showed subsequently that ammonium manganese phosphate dissolves in cold water, in hot water, and in an aqueous solution of ammonium chloride (1 : 70) to the extent of one part in 32,000, 1 part in 20,000, and 1 part in 18,000 respectively. It is clear, however, that the solubility of this precipitate is not indicated necessarily by the proportions given so long as an excess of the precipitant is present during the washing, though Fresenius did find in the filtrate traces of manganese which to his mind were sufficient to account for losses indicated by his test analyses, viz., 1 to 3 m.grms. of oxide, or from 2 to 6 m.grms. of phosphate.

Another mode of manipulation has been advocated by Blair (" The Chemical Analysis of Iron," p. 106) in order that the precipitate may be obtained more easily in crystalline condition. According to this method, dilute ammonia is added drop by drop, to the hot acid solution until the precipitate begins to form, the boiling and stirring are continued until the small amount of flocky precipitate is converted completely to crystalline condition, and the process of adding ammonia drop by drop is repeated until the manganese is all down in crystalline condition. The dilute ammonia is added in excess and the liquid filtered after cooling in ice-water.

In discussing these methods of precipitation, McKenna (*Jour. Anal. Chem.*, v., 141), points out that both give good and accordant results, and that the process may be carried on in glass as well as in platinum, if the time of crystallisation is made short enough.

When a manganous salt is precipitated in the cold by an excess of an alkaline phosphate, it falls, as Heintz (*Pogg. Ann.*, lxxiv., 449), has shown, in the form of the trimanganous phosphate of the formula $Mn_3P_2O_8$. This same phosphate constitutes, as we have found, the greater part of the precipitate which forms when a manganous salt reacts in the cold in the presence of ammonium chloride with microcosmic salt and ammonia in slight excess. Boiling or even subsequent standing may, as is well known, effect a more or less complete conversion of the manganese phosphate to the ammonium manganese phosphate. Thus, in one experiment in which an amount of manganous chloride enough to produce 0·2214 grms. of the pyrophosphate was precipitated in the cold by 5 c.m.^{3} of a saturated solution of microcosmic salt, with the subsequent addition of ammonia in excess, in a volume of 200 c.m.^{3} containing also 5 grms. of ammonium chloride, the residue after ignition weighed 0·1904 grms. Presuming this residue to consist entirely of the pyrophosphate and the trimanganous orthophosphate, the proportion of the former to the latter calculated from the relation of symbols, and the weights taken and found, is nearly one to six. That is to say, about six-sevenths of the precipitate fell in this experiment in the form of the tribasic orthophosphate. In another experiment made exactly similarly, excepting that the liquid was heated to boiling, the proportion of the manganese pyrophosphate to the trimanganous orthophosphate in the only partially crystallised precipitate proved to be two to one. That is, in this case, two-thirds of the precipitate was in the form of the pyrophosphate. In the former of the experiments a small amount of manganese was found in the filtrate, but not enough to change materially the ratio recorded. The slight solubility appears to be connected with the incomplete conversion of the trimanganous phosphate to the ammonium manganese phosphate, for, as will appear later, the manganese found in the filtrate, when the conversion is known to be nearly complete, is inappreciable unless extraordinary amounts of the ammonium salt are present. The success of the analytical process under discussion turns, therefore, upon the change of the trimanganous phosphate $Mn_2P_2O_8$ to the ammonium manganese phosphate NH_4MnPO_4. In the work to be described the attempt was made to learn the conditions under which this conversion may be best and most completely accomplished.

The conversion of a molecule of trimanganous phosphate to the ammonium manganese phosphate might be due, conceivably, either to the action of free ammonia or to the action of a salt of ammonium. The action of ammonia could only take place at the expense of a partial loss of manganese from the phosphate and its appearance as a hydroxide, two-thirds of the manganese going into two molecules of the ammonium manganese phosphate. In the presence of ammonium salts it is possible that the manganese oxide thus replaced might enter into union with the acid radical of the ammonium salt setting free ammonia; but if the ammonium salt present were the phosphate, or if an alkaline phosphate were present with other suitable ammonium salts, it is conceivable that the replaced manganese might appear as a constituent of a third molecule of ammonium manganese phosphate. In any event, it would be the ammonium salt and not the free ammonia which would determine the formation of the third molecule of the ammonium manganese phosphate. Plainly, too, the ammonium salt by itself, if it were a phosphate, or if a soluble phosphate were also present, might accomplish the conversion without the intermediate action of free ammonia. Unless, therefore, free ammonia favours the insolubility of the ammonium manganese phosphate, its presence would be unnecessary and might even be an actual disadvantage if the hydroxide naturally formed by its action upon the manganese phosphate were to fail to reunite fully with a phosphoric acid radical. It is plain, too, that the action of free ammonia might not stop with the replacement of one out of the three of the manganese atoms present in the molecule, but might even proceed under favourable conditions to the formation of phosphate richer in ammonium and to the separation of more manganese from its union with the acid radical. As a matter of fact Monro (*Am. Chem.*, 1877), has shown that the prolonged action of hot ammonia upon the precipitate produced by the interaction of a manganous salt and an alkaline phosphate does actually produce a hydroxide which blackens as it takes oxygen from the air. Our attention has been given, therefore, more especially to a study of the conditions of action under which a salt of ammonium —the chloride—may bring about the conversion of the precipitate first thrown down by an alkaline phosphate to the form of the ammonium manganese phosphate. Experiments were made upon solutions of pure manganous chloride prepared and standardised by means of the sulphate method, as described in a former paper (*Am. Journ. Sci.*, IV., v., 209), to show the effect of varying amounts of ammonium chloride on the condition of the precipitate and upon the solubility of the precipitate when once formed. The ammonium chloride for this work was prepared pure by boiling the chemically pure salt of commerce with a faint excess of ammonium hydrate and filtering—to free it from traces of iron, silica, and alumina. In the first series of experiments dilute ammonia was added slowly to the hot faintly acidulated solution containing the manganous chloride and more than enough, theoretically, of a saturated solution of microcosmic salt to precipitate the manganese present. The liquid was heated and stirred until the flocky mass was changed to a crystalline condition. The addition of ammonia drop by drop, with constant stirring and heating, was continued until the manganese was all precipitated in crystalline form. A slight excess of ammonia was added and the liquid with the precipitate was allowed to stand for half an hour, cooling gradually or chilled in ice water. The precipitate was filtered off on asbestos under pressure, washed carefully in water made faintly ammoniacal, dried, and ignited. The filtrates were tested for manganese by treatment with bromine and heating. The results of these experiments are given in Table I.

In this method of precipitation of the manganese in a pure solution of a manganous salt the results are all wrong. The proportion of the trimanganous phosphate to the pyrophosphate in the residue, calculated from the

TABLE I.

$Mn_2P_2O_7$ equivalent to $MnCl_2$.		Error in terms of $Mn_2P_2O_7$.	Error in terms of manganese.	Saturated solution of $HNH_4NaPO_4.4H_2O$.	Total volume.	Manganese in filtrate.
Taken. Grm.	Found. Grm.	Grm.	Grm.	C.m.^{3}.	C.m.^{3}.	
0·4033	0·3769	0·0264 –	0·0102 –	5	60*	None
0·4033	0·3728	0·0305 –	0·0118 –	5	60*	,,
0·3770	0·3530	0·0240 –	0·0090 –	5	60	,,
0·3770	0·3620	0·0150 –	0·0058 –	5	60	,,
0·4033	0·3751	0·0282 –	0·0109 –	10	60	,,
0·4033	0·3774	0·0259 –	0·0100 –	10	60	,,
0·4033	0·3871	0·0162 –	0·0062 –	5	200	,,
0·3226	0·3066	0·0160 –	0·0062 –	5	200	,,

* Chilled in ice-water.

TABLE II.

$Mn_2P_2O_7$ equivalent to the $MnCl_2$.		Error in terms of $Mn_2P_2O_7$.	Error in terms of manganese.	Saturated solution of $HNaNH_4PO_4.4H_2O$.	NH_4Cl.	Total volume.	Time of standing cold.	Manganese in the filtrate.
Taken. Grm.	Found. Grm.	Grm.	Grm.	C.m.^{3}.	Grms.	C.m.^{3}.	Hours.	
A.								
0·1542	0·1520	0·0022 –	0·0008 –	5	5	200	15	None
0·1542	0·1540	0·0002 –	0·0000 –	5	10	200	15	,,
0·1542	0·1536	0·0006 –	0·0002 –	5	10	100	5	,,
0·1542	0·1535	0·0007 –	0·0002 –	5	20	200	2½	,,
0·3770	0·3712	0·0058 –	0·0022 –	5	20	200	½	,,
0·3770	0·3724	0·0046 –	0·0018 –	5	20	200	½	,,
0·3084	0·3069	0·0015 –	0·0006 –	5	40	200	1	,,
0·3084	0·3060	0·0024 –	0·0009 –	5	40	200	1	,,
0·3084	0·3059	0·0025 –	0·0009 –	5	40	200	15	Trace
0·3084	0·3057	0·0027 –	0·0010 –	5	60	200	15	None
B.								
0·1542	0·1521	0·0021 –	0·0008 –	5	10	100	40	None
0·1542	0·1512	0·0030 –	0·0010 –	5	10	200	40	,,
0·1542	0·1532	0·0010 –	0·0003 –	5	20	200	15	,,
0·1542	0·1531	0·0011 –	0·0004 –	5	20	100	15	,,
0·3770	0·3720	0·0050 –	0·0019 –	5	20	200	½	,,
0·3770	0·3745	0·0035 –	0·0014 –	5	20	200	½	,,
C.								
0·1542	0·1519	0·0023 –	0·0009 –	5	15	200	—	None
0·1542	0·1530	0·0012 –	0·0004 –	5	20	200	—	,,
0·1542	0·1525	0·0017 –	0·0007 –	5	30	200	—	,,
0·3084	0·3020	0·0064 –	0·0025 –	5	10	200	—	,,
0·3084	0·3053	0·0031 –	0·0012 –	5	20	200	—	,,
0·3084	0·3033	0·0051 –	0·0020 –	5	20	200	—	,,
0·3084	0·3039	0·0045 –	0·0017 –	5	60	200	—	Trace

symbols and the weights taken and found, is in the average two to five; that is to say, five-sevenths of the trimanganous phosphate has been converted to the form of the ammonium manganous phosphate.

The precipitate obtained in this manner is white and granular, but not silky, and after ignition it shows the same dead white colour and is powdery. Evidently the regulation of the volume in which the precipitation is made is not essential, and the chilling of the liquid is of no importance in changing the manganese to the ammonium manganese salt under the given conditions. It is plain, moreover, that the assumption of a crystalline condition cannot serve as an indication that the composition of the salt is ideal. It is to be noted, however, that the conditions obtaining here are essentially different from those in common practice; for, ordinarily, when manganese is to be determined ammonium salts are abundantly present as the result of previous steps in analysis.

In the experiments of the next series the conditions are varied simply in this respect, that ammonium salts are introduced before the precipitation. The precipitate was less granular and more silky. After ignition the mass was white with a faint rose colour. In the experiments of Section A (Table II.) the precipitate first thrown down was re-dissolved, re-precipitated, and filtered after cooling; in those of Section B, the precipitate was filtered after cooling without re-solution and without re-precipitation; and in those of Section C, the first precipitate was filtered at once while the solution was still hot. The length of digestion before filtering and the indications of manganese in the filtrate are recorded in the table.

It was observed in these experiments that when the amount of ammonium chloride is present in considerable quantity a fine crystalline condition is got much more readily than when the amount of that salt is small: with maximum amounts of ammonium chloride the change from the flocky to the crystalline condition is almost immediate; even in the cold the change takes place to a marked extent in a few seconds. No manganese was found in the filtrate by boiling with bromine and ammonia —a test which is capable of indicating 0·0001 grm. of manganous sulphate in 500 c.m.^{3} of water containing 60 grms. of ammonium chloride—until the ammonium chloride amounted to 20 per cent of the mass, or to 40 grms. in 200 c.m.^{3} of the liquid, and even then but once in three trials: even when the proportion was 30 per cent —60 grms. in 200 c.m.^{3}—the solvent action of the ammonium chloride upon the manganese salt was trifling. The pyrophosphate residues obtained in these experiments, as well as in all those recorded in this paper, were dissolved in nitric acid and tested for contamination by a chloride; in no single case did silver nitrate produce more than an inappreciable opalesence in the solution. It is plain, therefore, that the variations of the results from theory are occasioned by variation in the degree of conversion of the trimanganese phosphate to the ammonium manganese phosphate, and that while the ammonium chloride shows no appreciable solvent action on the precipitate in the presence of the precipitant, its effect in the process of conversion is plainly evident. For the smaller amounts of the manganese salts (equivalent to 0·1542 grm. of the pyrophosphate) the effect of the ammonium chloride reaches a maximum when that salt amounts to 10 per cent of the solution; for twice that amount of manganese salt, the best results were obtained by doubling the amounts of ammonium chloride. Either line of treatment yields under the most favourable conditions, results which are passably good, but the advantage inclines slightly to the first method in which the first precipitate was dissolved and re-precipitated while the liquid was cooled before filtering.

(To be continued).

NOTICES OF BOOKS.

Arithmetical Chemistry. Part I., New Edition. By C. J. Woodward, B.Sc. London: Simpkin, Marshall, Hamilton, Kent, and Co., Ltd.

This little book sets forth, in simple language, the principles underlying the science of chemistry, and at the same time insists on the necessity of every pupil, even the youngest beginner, performing for himself such experiments as illustrate the principles dealt with in the text. After working conscientiously through this book, every student should be familiar with the arithmetical calculations involved in both quantitative and qualitative analysis.

It is to be regretted that the author does not distinguish between mass and weight. The statements on pages 15 and 42, if taken literally are irreconcilable. The confusion of terms is liable to involve the student in a confusion of ideas, which may easily lead to serious errors.

General Elementary Science. By William Briggs, M.A., F.R.A.S., F.C.S. Second Edition. London: W. B. Clive.

This volume forms part of the "University Tutorial Series" now being issued by Cambridge University. It treats, in simple language, of the elementary principles of Mechanics; Heat, Light, and Electricity; and Chemistry.

A handy volume, primarily intended for the use of Matriculation candidates, and should be useful to a larger circle of students.

The Organised Science Series. Second Stage Mathematics. Edited by William Briggs, M.A., &c. London: W. B. Clive.

This book is compiled specially to meet the needs of students preparing for the advanced stage of the Science and Art Examinations. Being intended for the use of students without the personal help of a tutor, the various problems and theorems are worked out with an unusual amount of detail, and any ordinary student should with this guide be able to pass the examination with ease.

Section I., dealing with Euclid, Books II., III., and IV., calls for no comment, excepting that an alternative solution to Prop. I., Book III., on page 39, is not valid, since it is not known at this stage that more than two of the lines bisecting chords of a circle at right angles meet at the same point. Exercise 6, on page 43, is curiously worded; in fact, as it stands it has no solution, since, in general, a circle cannot be described through four given points.

Section II. deals with Algebra, chiefly quadratic equations. This section should be carefully edited in future editions, and the misplaced and dropped signs—especially numerous in Chapter 4—corrected.

Section III. treats of the elements of trigonometry and the principles and use of logarithmic tables in a clear manner, though this section could with advantage be compressed.

On the whole the work is well adapted to its purpose, though there is room for improvement in future editions.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvi., No. 26, June 27, 1898.

Action of Hydrogen on Sulphide of Silver and the Inverse Reaction.—H. Pélabon.—The author investigates the reaction of sulphuretted hydrogen and silver or of hydrogen and silver sulphide contained in sealed tubes at a fixed temperature. After a measured time the tube is quickly cooled and the gases are analysed. He finds (1) that for temperatures above 350° C. the limiting values for the proportion of sulphuretted hydrogen in the mixture are identical, whether the tube originally contained H_2S and silver or Ag_2S and hydrogen; and (2) that equilibrium is obtained in a time, increasing as the temperature is lowered. The silver is deposited in the form of threads when the temperature is below 580°; at higher temperatures the particles of silver sulphide are seen at the end of the experiment to be covered with an almost uniform layer of metallic silver.

Heat of Formation of Lithium Carbide.—M. Guntz.—This is found by measuring the heat evolved by the solution of a known weight of lithium carbide in water—

$$C_2Li_2 + 2H_2O = 2LiOH + C_2H_2.$$

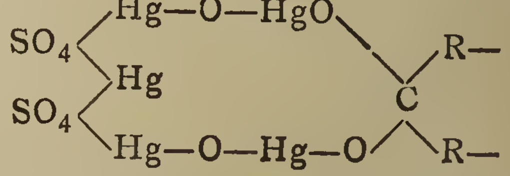
The number found (37·1 cal.) is the mean of three determinations. In order to avoid the correction due to the solubility of acetylene in the liquid in the calorimeter, the decomposition takes place in a glass apparatus, plunged into the calorimeter, from which the acetylene escapes freely into the air. The quantity of carbide employed is found each time by titration. The heat formation of Li_2C_2 is much greater than the corresponding values for CaC_2 and NaC_2.

Capacity of Organic Bodies for Combining with Mercuric Sulphates. The Case of the Acetones.—G. Denigès.—In a preceding communication the author has demonstrated the facility with which $HgSO_4$ furnishes well-defined insoluble compounds with thiophene and the ethylene hydrocarbons. The following table enumerates the principal bodies which have yielded such compounds—

Thiophene and its derivatives.
Ethylene, benzene, terpene, and their derivatives.
Aldehyds.
Acetones.

Fatty acetones heated to boiling with large excess of $HgSO_4$ yield bodies insoluble in water corresponding to the general formula—

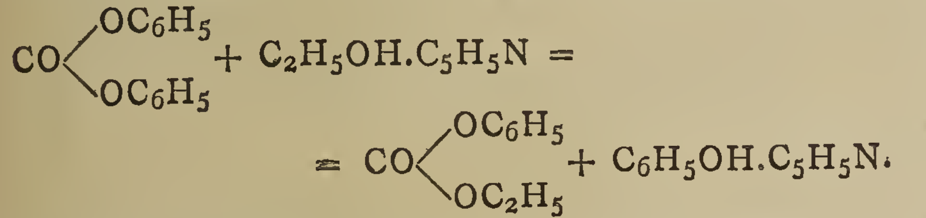
$(HgSO_4)_2 3HgO.COR_2 =$



$$SO_4\left\langle\begin{array}{l}Hg—O—HgO\diagdown \\ \;\;Hg \\ \end{array}\right. \qquad SO_4\left\langle Hg—O—Hg—O\diagup\right.C\left\langle\begin{array}{l}R— \\ R—\end{array}\right.$$

With ordinary acetone the reaction is absolutely quantitative. Secondary actions occur in the case of acetones richer in carbon.

A General Method for Preparing Mixed Carbonic Esters of the Fatty and Aromatic Series.—P. Cazeneuve and Albert Morel.—Fatianow, Richter, and Bender obtained carbonic esters of ethyl and different phenols by means of the reaction between ethyl chlorocarbonate and phenolates of sodium or potassium. The author has succeeded in producing these mixed carbonates in a more practical way by warming neutral phenolic carbonates with different alcohols in presence of certain organic bases. Phenyl carbonates in particular, warmed with fatty alcohols in presence of urea, give mixed carbonates of phenyl and the alcohol in question. Certain of these esters have been obtained extremely pure, but the higher members are difficult to purify on account of the formation of urethanes. Other bases act similarly to urea without giving rise to these impurities, *e.g.*, aniline, dimethylaniline, pyridine, and quinoline. The double decomposition which occurs is, according to the following equation—



$$CO\begin{matrix}\diagup OC_6H_5\\ \diagdown OC_6H_5\end{matrix} + C_2H_5OH.C_5H_5N =$$
$$= CO\begin{matrix}\diagup OC_6H_5\\ \diagdown OC_2H_5\end{matrix} + C_6H_5OH.C_5H_5N.$$

The decomposition is hastened by the affinity of the base for phenol. Further, a similar reaction occurs between sodium ethylate dissolved in excess of absolute alcohol and phenyl carbonate.

Vol. cxxvii., No. 1, July 4, 1898.

Decomposition of Water by the Salts of Protoxide of Chromium, and the Employment of these Salts for the Absorption of Oxygen.—M. Berthelot.—At temperatures below 250° a solution of chromous chloride, quite pure and free from all tracs of acid, does not decompose water, even when the two are left in contact for eleven years. At temperatures above 250° the water is decomposed. However, chromous chloride can be made to decompose water at ordinary temperatures. With the help of some outside energy, for example, the slightest addition of HCl, the decomposition takes place even in the cold. This decomposition only proceeds up to a certain point, for after two months the liquid is found still to contain two-fifths of the chromous chloride unaltered.

Action between Free Hydrogen and Nitric Acid.—M. Berthelot.—Hydrogen and nitric acid react on one another in an unexpected way. They exert no reciprocal action in the cold, nor at 100°, even under conditions when nitric acid would decompose of itself, giving off oxygen. A little bulb containing pure nitric acid is put in a vessel filled with hydrogen and sealed off; the bulb is broken and the tube placed horizontal and exposed to solar light for some days. The gases are then examined and the hydrogen is found to be unaltered in amount, the oxygen present being formed by the decomposition of the nitric acid only. An almost equal amount of oxygen is formed if the hydrogen is not present at all. If two similar tubes containing nitric acid are placed in darkness, in one pure hydrogen, the other a vacuum, in neither case does any change take place. This inactivity between nitric acid and hydrogen ceases at a high temperature.

Preparation and Properties of Hydride of Calcium.—Henri Moissan.—The author prepares this substance from pure crystalline calcium, which is put in a nickel boat in a glass tube, through which passes a current of pure dry hydrogen. At ordinary temperatures no action takes place and the hydrogen merely sweeps out the tube. The tube is then sealed off and the hydrogen kept under a pressure of 30 to 40 c.c. of water. The temperature is raised to dull redness, when the calcium is seen to take fire in the atmosphere of hydrogen. The gas is rapidly absorbed and the calcium metal is transformed into white hydride of calcium. The hydride has sp. gr. 1·7 and has the appearance of small thin transparent plates. It is stable up to 600° in a vacuum and has a formula CaH_2.

Blue Glass with Chromium Bases.—André Duboin.—Already inserted.

Seleniate of Copper and its Employment in the Preparation of Selenic Acid.—R. Metzner.—Seleniate of copper is prepared by passing a current of chlorine through an aqueous solution of SeO_2 :—

$$SeO_2 + 2Cl + H_2O = 2HCl + SeO_3.$$

The acid is then neutralised by oxide of copper, when the liquid takes a blue colour. Analysis shows the seleniate of copper to have the formula $2(CuOSeO_3)CuO5H_2O$.

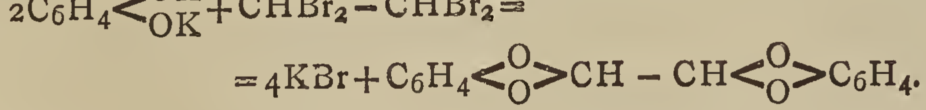
The Phenyl Urethanes of the Ethers and Nitrates of certain Oxyacids.—E. Lambling.—Following the observation of A. W. Hofmann, that phenylisocyanate combines readily with alcohols and phenols to give urethanes, the author proposes to investigate the effect that may be exercised on the alcoholic hydroxyl by the proximity of various acidifying groups, such as C_6H_5, CN, CO, &c. The possible influence of these radicals is studied by the action of phenylisocyanate on bodies of analogous constitution, viz.:—(1) Lactic ether and trichloracetic ether, and nitrile; (2) glycolic ether and nitrile; (3) phenylglycolic ether and nitrile; (4) β-oxybutyrate of ethyl and α-oxyisobutyrate of ethyl. A description of the preparation and composition of the urethanes of these substances is given, and the conclusion drawn that the groups CN, C_6H_5, CO, CCl_3, exercise no sensible influence in the fixation of the phenylisocyanate by the neighbouring hydroxyl; also that it apparently does not matter whether the alcoholic hydroxyl be primary, secondary, or tertiary.

A New Combination of Acetylene with an Oxychloride of Copper, corresponding to the Formula C_2H_2—$Cu_2Cl_2.Cu_2O$.—R. Chavastelon.—The author prepares the compound in two ways:—(1) By allowing a crystal of $C_2H_2.Cu_2Cl_2$ to stand in contact with distilled boiled out water at ordinary temperatures, the change not being complete for several days; (2) by adding to excess of water a solution of $C_2H_2.Cu_2Cl_2$ crystals, or a solution, saturated with acetylene, of Cu_2Cl_2 in hydrochloric acid, in which case an abundant violet flocculent precipitate is at once obtained. The formation of this compound is accompanied by evolution of acetylene and production of free hydrochloric acid, and by determining the quantities of these two substances produced when a known weight of $C_2H_2Cu_2Cl_2$ is treated with water, the composition of the residue is deduced. A more exact method of determining the composition is to analyse the substance formed, which is found to correspond to the formula $C_2H_2.Cu_2Cl_2.Cu_2O$.

Ethane Di-pyrocatechin.—Ch. Moureu.—The author investigates the action of dibrom- and tetrabromacetylene on pyrocatechin in the presence of alkalis. With $C_2H_2Br_2$, spontaneously inflammable C_2HBr is evolved, and no $C_6H_4O_2.C_2H_2$; but with $C_2H_2Br_4$, on the contrary, a well-defined condensation product with pyrocatechin is formed. Its composition agrees with the formula $C_{14}H_{10}O_4$, *i.e.*, ethane-di-pyrocatechin—

$$C_6H_4O_2 = C_2H_2 = C_6H_4O_2,$$

which is formed according to the equation—



$$2C_6H_4{<}^{OK}_{OK} + CHBr_2 - CHBr_2 =$$
$$= 4KBr + C_6H_4{<}^{O}_{O}{>}CH - CH{<}^{O}_{O}{>}C_6H_4.$$

A description of the properties of this substance is given.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 7th inst., Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, presiding. The special thanks of the Members were returned to Mr. John B. Carrington, for his donation of £25, and to Mr. Charles Scott Dickson, Q.C., Solicitor-General for Scotland, for his donation of £100 to the fund fer the promotion of Experimental Research at Low Temperatures.

MEETINGS FOR THE WEEK.

Wednesday, 16th.—Microscopical, 7.30. Exhibition of Shum's Slides of Diatoms Mounted in High Refractive Media.

Thursday, 17th.—Chemical, 8. "Preparation of Hyponitrite from Nitrite through Oxyamidosulphonate," by E. Divers, M.D., F.R.S., and T. Haga, B.Sc. "Absorption of Nitric Oxide in Gas Analysis," "Interaction of Nitric Oxide with Silver Nitrate," "Preparation of Pure Alkali Nitrites," "The Reduction of an Alkali Nitrite by an Alkali Metal," "Hyponitrites—their Preparation by Sodium or Potassium and Properties," by E. Divers, M.D., F.R.S.

THE CHEMICAL NEWS.

VOL. LXXVIII., No. 2034.

THE ESTIMATION OF FORMIC ACID IN THE PRESENCE OF ACETIC ACID, AND OF EASILY OXIDISABLE BODIES.

By ALEXANDRE LEYS.

THE estimation of formic acid in the presence of other organic bodies, such as acetic acid or alcohol, presents difficulties of a special nature. Distillation only effects a partial separation, and the direct use of oxidising agents is in most cases impossible.

M. F. Freyer gave, some years ago, in the *Chemiker Zeitung* (No. 51, 1895), a process for the titration of formic acid in acetic solution; but this process loses all its value when the materials are not absolutely pure, and it is quite inapplicable in the presence of alcohol.*

We have found a reaction which enables us to overcome these difficulties, and to estimate with exactitude formic acid mixed either with acetic acid, methylic or ethylic alcohol, or even with their corresponding aldehyds. There is no doubt that, later on, we shall be able to add to this necessarily limited list.

If we take a solution of acetate of mercury, and pour into it minimal quantities of formic acid, no reaction appears to take place at ordinary temperatures. The mixture remains clear, and it is only after a few hours that pearly-looking scales, of great lightness, begin to deposit in the flask, which must be kept closed to prevent all evaporation. These are crystals of mercurous acetate, of which the deposition increases during from eight to fifteen days, according to the surrounding temperature and the quantity engaged in the reaction. We also noticed that small bubbles of gas become disengaged from the mass.

With larger quantities of formic acid the manner of the reaction does not change; no cloudiness is observed when the mixture with the mercuric acetate is made, but the deposit takes a shorter time to produce, and, instead of forming light pearly flakes, it seems to differ slightly, and takes the form of a white pulverulent precipitate.

This reaction, slow to finish at the ordinary temperature, takes place with rapidity when we heat to boiling. We notice the bubbles of gas, more and more numerous, deposited on the sides of the glass, and the liquid even appears to be boiling, although that temperature may not be nearly reached. The heat must be stopped as soon as boiling commences, and already we see light flaky crystals floating on the surface. On cooling, the whole volume of the liquid becomes full of a mass of crystals with a brilliant white lustre.

The presence of acetic acid, alcohol, or of aldehyd in no way interferes with this reaction, but when their proportions become considerable the volume of the precipitate varies. The crystals are more granular, more dense, and do not occupy the whole space. Nevertheless, repeated analyses that we have made have always shown the same proportion between the acting formic acid and the quantities of mercury found in the state of mercurous salts.

We therefore believe, although we have not yet verified it, that we have to do with two kinds of crystals of mercurous acetate, one of which at least contains a certain quantity of water. But, however this may be, the reaction is always complete when we reach the boiling-point of the mixture; and in fact in the various cases, if we separate the crystals by filtration, the filtered liquid will not become cloudy even after the lapse of several days.

According to our ideas the following is what happens:—The formic acid displaces the acetic acid from the mercuric acetate, and gives a mercuric formate which is unstable and changes spontaneously into mercurous formate. The mercurous formate is in its turn attacked by the acetic acid, and a very slightly soluble mercurous acetate is formed, which crystallises out. This reaction can be shown in the following manner:—

$$2\genfrac{}{}{0pt}{}{\mathrm{CH_3COO}}{\mathrm{CH_3COO}}\!>\!\mathrm{Hg}+4\mathrm{H.COOH}=$$
$$=4\mathrm{CH_3.COOH}+2\genfrac{}{}{0pt}{}{\mathrm{H.COO}}{\mathrm{H.COO}}\!>\!\mathrm{Hg}$$

$$2\genfrac{}{}{0pt}{}{\mathrm{H.COO}}{\mathrm{H.COO}}\!>\mathrm{Hg}=\genfrac{}{}{0pt}{}{\mathrm{H.COO}}{\mathrm{H.COO}}\!>\!\mathrm{Hg_2}+\mathrm{H.COOH}+\mathrm{CO_2}$$

$$\genfrac{}{}{0pt}{}{\mathrm{H.COO}}{\mathrm{H.COO}}\!>\mathrm{Hg_2}+2\mathrm{CH_3.COOH}=$$
$$=\genfrac{}{}{0pt}{}{\mathrm{CH_3COO}}{\mathrm{CH_3COO}}\!>\!\mathrm{Hg_2}+2\mathrm{H.COOH}.$$

The destruction of a single molecule of formic acid suffices to accomplish this cycle, and 1 molecule of mercurous acetate is deposited.

Let us add that the chief characteristic of this reaction is that it takes place with the smallest quantities of formic acid; 10 m.grms. in a solution of mercuric acetate produce a voluminous precipitate, even in the cold. To easily repeat the experiments we have just described, it is necessary to use solutions of formic acid at 1 per cent; a stronger solution would not give such good results.

We take a Bohemian glass flask gauged to 100 c.c., and pour in 10 c.c. of the acid solution, 20 c.c. of a 20 per cent solution of mercuric acetate, and make up to 100 c.c. with distilled water; then boil, stop the heat as soon as the boiling-point is reached, and allow to cool slowly.

After having recognised by numerous analyses that the precipitation of a molecule of mercurous acetate really corresponded with the destruction of H—CO.OH, and having found a convenient method for weighing the mercurous salt produced, we decided on the following method of estimation, which is perfectly exact:—

The Case of a Mixture of Acetic and Formic Acids.—We commence by the determination of the acidity of the mixture in terms of acetic acid. Here it is necessary to distinguish between two possible cases:—

Case I.—The mixture is rich in acetic acid, and contains only a small quantity of formic acid. We dilute with water until the mixture contains only 20 to 30 per per cent of acids.

Case II.—The mixture reaches the proportion of 1 part of formic acid for 20 parts of acetic acid. For this proportion and for all higher proportions (of formic acid) we dilute with water until the liquid has an acidity of only 2 per cent. Having obtained a sufficiently dilute solution, we take 10 c.c. and place them in a beaker having a mark for 100 c.c. at about one-third of its height, we add 20 or 30 c.c. of a 20 per cent solution of mercuric acetate, and fill up to the mark with distilled water.

The relatively large quantity of mercuric acetate thus present is necessary, for we found that the mercurous salt produced is not stable except in the presence of such an excess. When the proportion is not sufficient it easily decomposes, and becomes of a greyish colour and loses mercury.

We then heat so as to reach the boiling-point in seven or eight minutes; as soon as this temperature is reached we withdraw the flame, and leave the whole to cool until the following day. The product thus obtained is of a

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* Besides Freyer's process—which is an application of the experiments made by Chapman and Thorp on the non-oxidation of acetic acid, even at 100°, by chromic acid—there exists a method of estimating formic acid when mixed with acetic acid, which is due to MM. Portes and Ruyssen. This process has been modified by M. Scala (*Gazz. Chim. Ital.*, 1890, p. 393). M. Lieben, who has studied this latter method, gives it the following character:—The reaction is always very slow in finishing, which leads to losses of formic acid. We can only arrive at approximately exact results by using a large excess of mercuric chloride. M. Lieben recommends four times the theoretical weight, or fifty times the weight of the formic acid, and heating for from six to eight hours.

brilliant white colour: it is collected in a funnel plugged with a little glass wool, and the portions adhering to the sides of the beaker are washed in by means of the filtrate which is poured back into the glass in which the reaction took place. When the beaker no longer contains any trace of the precipitate the funnel is allowed to drain; we then wash four or five times with alcohol at 95° containing 2 c.c. per cent of glacial acetic acid. This slight acidity prevents the solution of mercuric acetate which impregnates the crystals from being decomposed by the strong alcohol, and thus permits a complete washing of the deposit. We finish by two or three washings on the funnel with neutral alcohol at 95°, to remove all trace of acetic acid, and we finally get rid of the alcohol with a few washings with anhydrous ether.

The product is allowed to dry either in free air or under a bell-jar *in vacuo*, and we obtain on the funnel a felted mass of beautiful silvery-white crystals, somewhat resembling the flakes of boric acid. These crystals are quickly dissolved in nitric acid diluted with its own volume of water.

To obtain good results it is necessary that the reaction should be almost instantaneous, so as to prevent a slight precipitation of mercury; but, however, even if the precipitate is produced, the quantity of mercury precipitated is so minute that the error may be neglected. Further, this slight loss disappears of itself after standing a few hours.

The funnel and its contents are plunged into nitric acid, then withdrawn and washed thoroughly. Make up to a given volume, and there then remains nothing but to estimate the mercury in the state of a mercurous salt in the solution.

Take 10 c.c. of the solution of mercurous nitrate, dilute with a large quantity of water, and precipitate with a slight excess of chloride of sodium. After standing a sufficiently long time, so that the supernatant liquid may become clear, the mercurous chloride is collected on a tared filter. Wash until the filtrate is neutral, and place the precipitate in an oven at 100°; it is important that the mercurous chloride should not be exposed to the temperature of 100° longer than is absolutely necessary to properly dry it, for we have observed that even at this temperature there is a sensible volatilisation of the substance. The following table will prove this:—

	Weight of precipitate.	Losses.
1st day	0·066 grm.	—
2nd ,,	0·061 ,,	5 m.grms.
3rd ,,	0·056 ,,	10 ,,
4th ,,	0·051 ,,	15 ,,
5th ,,	0·047 ,,	19 ,,

We multiply the weight of the mercurous chloride found by 0·0976 to obtain the corresponding weight of formic acid. The factor 0·0976 is obtained by the following reasoning:—The destruction of 1 molecule of formic acid leads to the precipitation of 1 molecule of mercurous acetate; but for the purpose of estimation this latter was converted into chloride; therefore—

$$474\,x = 46,$$

$$\text{whence}\quad x = 0{\cdot}0976.$$

The different samples of formic acid we have tried have given us results absolutely concordant. We bring them all first to a strength of 1·30 per cent of total acidity; we then take 10 c.c., or 0·130 grm., which we place in the reaction beaker, adding 2 c.c. of glacial acetic acid before completing with the mercury salt and water.

The following is a series of results:—

First result	0·132 grm.
Second ,, ...	0·129 ,,
Third ,, ...	0·1289 ,,
Fourth ,, ...	0·1288 ,,

This table shows the results obtained with a mixture of 2 parts of acetic acid and 0·130 part of formic acid, or, in other words, with an acetic acid containing 93·9 per cent of acetic acid and 6·1 per cent of formic acid. Experiments we have made authorise us to state that we could obtain as exact results with an acid containing 99 per cent of acetic acid and 1 per cent of formic acid.

The Case of a Mixture of Formic Acid and Alcohol.—After having determined the acidity, we dilute with water to bring the liquid to from 1 to 2 per cent. Pour 10 c.c. into the gauged beaker, then before adding the mercuric acetate we add 2 c.c. of glacial acetic acid to check the precipitation. We then proceed as before, and we obtain the substance already described, or, when the proportion of alcohol is considerable, granular, dense crystals of which we have already spoken. In every way the results are just as exact. For 0·130 grm. of acid put in reaction in alcohol at 30° we found 0·129 grm.

The Case of a Mixture of Formic Acid, Acetic Acid, and Alcohol.—We operate as before, but without adding acetic acid when the proportion in the solution is already great.

All that we have said with regard to ethylic or methylic alcohols will apply to their aldehyds pure or mixed with them. We are strongly inclined to think—but as we have not verified it we cannot state definitely—that many other organic bodies could be present without interfering with the reaction.

Without wishing to dwell too long on the applications of which this reaction is susceptible, we will, however, just mention the following:—The determination of small quantities of formic acid which are to be found in certain raw spirits, and by that means detecting adulteration. The determination of quantities of formic acid, which, mixed with acetic acid, are found in commercial formol. A method of titrating formic aldehyd after oxidation. Finally, a method of testing and titrating methylic alcohol mixed with the alcohol in wines, when we are in possession of a method of oxidation which will transform the alcohols into acid without attacking these latter.—*Moniteur Scientifique*, Series 4, xii., Part 2, Sept., 1898.

ON THE DETERMINATION OF MANGANESE AS THE PYROPHOSPHATE.*

By F. A. GOOCH and MARTHA AUSTEN.

(Concluded from p. 242).

In Table III. are recorded results obtained by precipitating the cold acid solution of the manganese salt and the microcosmic salt with a strong excess of ammonia. The mixture was heated to boiling for from five to ten minutes and filtered hot. In this series of determinations the amount of ammonium chloride present was constant, while the volume of the liquid present was varied and the amounts of the microcosmic salt.

These results are possibly a trifle less satisfactory than those obtained for the smaller amounts of manganese by the method of Table II., it may be because the prolonged boiling tends to form a trifling amount of free oxide; but the fact is disclosed that an increase of the microcosmic salt is without influence, and that a variation in volume from 200 c.m.^{3} to 300 c.m.^{3} is the occasion of little change in the indications of the process.

In another series of experiments the solution of manganous chloride was added drop by drop to the mixture of microcosmic salt and ammonium chloride made alkaline with ammonia. The precipitate which fell in the cold was crystallised by boiling the mixture a few minutes. The results are given in Table IV.

The experience of this series of experiments demonstrated again that the ease with which the flocky precipitate is converted to the crystalline ammonium manganese

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* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, 1898, vol. vi., p. 233.

Table III.

$Mn_2P_2O_7$ equivalent to $MnCl_2$.		Error in terms of $Mn_2P_2O_7$.	Error in terms of manganese.	Saturated solution of $HNaNH_4PO_4.4H_2O$.	NH_4Cl.	Total volume.	Manganese in the filtrate.
Taken.	Found.						
Grm.	Grm.	Grm.	Grm.	C.m.³.	Grms.	C.m.³.	
0·2214	0·2202	0·0012 −	0·0005 −	5	20	200	None
0·2214	0·2202	0·0012 −	0·0005 −	5	20	200	,,
0·2214	0·2191	0·0023 −	0·0009 −	5	20	200	,,
0·2214	0·2191	0·0023 −	0·0009 −	5	20	300	,,
0·2214	0·2191	0·0023 −	0·0009 −	5	20	300	,,
0·2214	0·2185	0·0029 −	0·0011 −	10	20	200	,,
0·2214	0·2186	0·0028 −	0·0010 −	20	20	300	,,
0·2214	0·2192	0·0022 −	0·0009 −	20	20	300	,,

Table IV.

$Mn_2P_2O_7$ equivalent to $MnCl_2$.		Error.	Error in terms of manganese.	Saturated solution of $HNaNH_4PO_4$.	NH_4Cl.	Total volume.	Manganese in the filtrate.
Taken.	Found.						
Grm.	Grm.	Grm.	Grm.	C.m.³.	Grms.	C.m.³.	
0·1542	0·1521	0·0021 −	0·0008 −	5	5	200	None
0·2214	0·2203	0·0011 −	0·0004 −	5	10	275	,,
0·2214	0·2192	0·0022 −	0·0009 −	5	15	275	,,
0·2214	0·2197	0·0017 −	0·0007 −	5	20	275	,,
0·2214	0·2223	0·0009 +	0·0003 +	5	20	200	,,
0·1542	0·1528	0·0014 −	0·0005 −	5	30	275	,,

Table V.

$Mn_2P_2O_7$ equivalent to MnO_2.		Error in terms of $Mn_2P_2O_7$.	Error in terms of manganese.	Saturated solution of $HNaNH_4PO_4$.	NH_4Cl.	Total volume.	Manganese in the filtrate.
Taken.	Found.						
Grm.	Grm.	Grm.	Grm.	C.m.³.	Grms.	C.m.³.	
			A.—*In Platinum.*				
0·1885	0·1903	0·0018 +	0·0007 +	5	20	200	None
0·1885	0·1910	0·0025 +	0·0010 +	5	20	200	,,
0·1885	0·1913	0·0028 +	0·0011 +	5	20	200	,,
0·1885	0·1911	0·0026 +	0·0010 +	5	20	200	,,
0·3770	0·3776	0·0006 +	0·0002 +	5	20	200	,,
0·3770	0·3773	0·0003 +	0·0001 +	5	20	200	,,
0·3770	0·3778	0·0008 +	0·0003 +	5	20	200	,,
0·3770	0·3783	0·0013 +	0·0005 +	5	20	200	,,
			B.—*In Glass.*				
0·1885	0·1904	0·0019 +	0·0007 +	5	20	200	,,
0·1885	0·1898	0·0013 +	0·0005 +	5	20	200	,,
0·3770	0·3767	0·0003 −	0·0001 −	5	20	200	,,
0·3770	0·3784	0·0014 +	0·0005 +	5	20	200	,,

phosphate is proportioned to the ammonium chloride present, and the mean error of the results for the phosphate when the ammonium chloride reached 20 grms. (−0·0007 grm.) is considerably less than the mean error (−0·0018 grm.) when the amount of the ammonium salt was less than 20 grms.

Experiments were also made according to the modifications suggested by Munroe (*loc. cit.*), viz., the boiling of the manganous salt with an excess of microcosmic salt until the precipitate becomes crystalline and just neutralising with dilute ammonia; but we have been unable to find the conditions of this treatment by which uniform results may be obtained in even moderate agreement with the theory.

We have tried also the effect of substituting ammonium nitrate for ammonium chloride in the conversion process; but, so far as our experience goes, the nitrate is not so effective weight for weight in producing the change of the trimanganous phosphate to the ammonium manganese phosphates, while the solubility of the product in the solution of the ammonium nitrate becomes appreciable more rapidly with the increase of the amount present than is the case when the ammonium salt is the chloride.

In the light of the experiments described it would seem to be reasonable to expect the best results from the phosphate method for determining manganese when the conditions are so arranged that precipitation may take place in the cold solution in the presence of but little free ammonia, and of enough ammonium chloride to bring about the rapid conversion of the precipitate to the crystalline condition. Under such circumstances it should be possible to secure the conversion of the phosphate to the ideal constitution as completely as possible without danger of subsequent decomposition by the prolonged action of the hot free ammonia. In carrying out this idea, the solution of manganese chloride was treated, as before, with microcosmic salt and a large amount of ammonium chloride, the precipitate first formed was re-dissolved in hydrochloric acid, and precipitation again brought about by the very careful addition of dilute ammonia in slight but distinct excess. The mixture was heated only until the precipitate became silky and crystalline, when it was allowed to stand and cool for a half hour. The precipitate was filtered off upon asbestos in a perforated platinum crucible under pressure, ignited, and weighed. Table V. comprises the results of experiments made in this manner. In those of Section A the precipitation was made in platinum vessels; in those of Section B the treatment was in glass.

In this series of experiments the mean indication is, for the first time, in excess of the theory. Previously the error has been one of deficiency, and that in proportion to the amount of manganese handled, no doubt because the amount of unconverted trimanganese phosphate is proportioned to the entire amount of the phosphate. The positive error which is developed in this last series of determinations is probably due to the appearance of the natural error of all precipitation processes — viz., the tendency on the part of the precipitate to include matter in solution. In the previous experiments this effect was doubtless obscured by the incompleteness of the conversion of the trimanganous phosphate to the ammonium manganese phosphate. Indeed, it is quite possible that even in the last determinations the conversion is not absolute, and that this is so suggested by the fact that the errors of excess are larger in the case of the smaller amounts of manganese for which the conversion throughout the entire work has appeared to be more complete. From the consideration of the results tabulated and described it would seem to be obvious that not only is the presence of ammonium chloride not objectionable in this analytical process, which depends upon obtaining the ammonium manganese phosphate from the trimanganese phosphate precipitated from a pure solution of manganese, but that its presence in not too small amount, or that of a substitute, is absolutely essential to make this conversion complete. For a given amount of manganese and a given volume of solution it seems essential that the amount of ammonium chloride should reach a certain limit. According to our experience the proportion of ammonium chloride to the pyrophosphate should be at least 50 : 1; or, speaking approximately, more than 200 molecules of ammonium chloride must be present in the liquid (100 c.m.^{3} or 200 c.m.^{3}) to every molecule of the ammonium manganese phosphate to be formed. However, the quantity of the ammonium salt may be increased almost to the point of saturation of the liquid without causing more than a trifling solubility of the ammonium manganese phosphate in the presence of an excess of the precipitant. The statement of Fresenius and Munroe that ammonium manganese phosphate is soluble in ammonium chloride does not hold if there is an abundance of the soluble precipitating phosphate present. Further, our experience goes to show that the precipitate may be washed with perfect safety with pure water as well as with slightly ammoniacal water, or with ammoniacal water containing ammonium nitrate, if the filtration is performed rapidly and the precipitate is gathered in small space, as is the case when the phosphate is collected on asbestos in a perforated crucible. The finely granular precipitate which may be obtained by slow action of dilute ammonia added gradually to the hot solution of the manganese salt apparently includes a portion of unconverted phosphate which resists the replacement of the manganese by ammonium. On the other hand, the precipitate of flocky condition thrown down in the cold passes easily to the silky and crystalline condition when heated with the proper amount of ammonium salt and possesses a constitution approaching the ideal under such conditions. The conversion of the flocky manganous phosphate is so rapid that the precipitation may be carried on safely in glass vessels. If the ammonium chloride in the solution were to be included in the precipitate it would volatilise entirely during the ignition, leaving no trace unless, possibly, a portion of its chlorine were to combine with the manganese. Tests for chlorine in the residue of pyrophosphate resulted negatively—no more than a mere trace being found in any case, so that the contaminating effect of the ammonium chloride proves to be insignificant, and the responsibility for the increase in weight above the theory must apparently rest with the included microcosmic salt.

In the practical determination of manganese by the phosphate method of Dr. Gibbs, therefore, we advocate strongly the presence of large amounts of ammonium chloride. Good results may be obtained by the method of precipitation originally laid down by Dr. Gibbs, or by the modification proposed by Blair, if the ammonium salt is present in sufficient quantity. On the whole, trustworthy results are obtained most easily and surely, according to our experience, by following the method of the experiments of Table V. The slightly acid solution, containing in a volume of 200 c.m.^{3} (in platinum or glass) an amount of manganese not more than enough to make 0·4 grm. of the pyrophosphate, 20 grms. of ammonium chloride, and 5 to 10 c.m.^{3} of a cold saturated solution of microcosmic salt, is precipitated in the cold by the careful addition of dilute ammonia in only slight excess. The mixture is heated until the precipitate becomes silky and crystalline, the whole is allowed to stand and cool a half hour, the precipitate is collected upon asbestos in a perforated platinum crucible, washed (best with slightly ammoniacal water), dried at gentle heat, and ignited as usual. By this process determinations of the larger amounts of manganese—0·4 grm. of the pyrophosphate—approximate rather more closely to the theoretical values than do those of the smaller amounts—0·15 grm. In either case the average error should not exceed 0·0010 grm. in terms of manganese.

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending October 31st, 1898.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To Major-General A. De Courcy Scott, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, November 7th, 1898.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Oct. 1st to Oct. 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined by us during the month all were found to be clear, bright, and well filtered.

The rainfall at Oxford during the month of October has been 4·59 inches; as the average for the last thirty years is only 2·57 inches, we have an excess of 1·84 inches. This reduces the deficiency for the year to 6·38 inches, or 30·09 per cent.

Our bacteriological examinations of 257 samples have given the results recorded in the following table; we have also examined 55 other samples, from special wells, standpipes, &c., making a total of 312 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	1234
New River, filtered (mean of 26 samples) ..	22
Thames, unfiltered (mean of 26 samples) ..	8804
Thames water, from the clear water wells of five Thames-derived supplies (mean of 127 samples) ..	28
Ditto ditto .. highest	316
Ditto ditto .. lowest	0
River Lea, unfiltered (mean of 26 samples) ..	1719
River Lea, from the East London Company's clear water well (mean of 26 samples) ..	13

The average daily flow of the Thames over Teddington Weir, for the present year to the end of the drought, is 550 million gallons, as compared with 826 million gallons, the average daily flow for the same period during the ten preceding years. Thus there has been a deficiency of one-third in the average daily flow of the river since the beginning of the year to October 17th, when the drought ended.

The extraordinary drought—the most severe for at least 40 years—having ended, there are several matters which deserve consideration. The average bacteriological condition of the raw, unfiltered Thames and Lea waters during that period was exceptionally good, seeing that the bulk of the supply was spring water. The condition of the filtered water supplied to London was excellent, and in the case of the East London supply the quality was substantially the same as during similar seasons when the supply of water was ample.

The large rainfall which took place in October has had the effect of suddenly washing into the rivers organic matter accumulated on the water-shed during the three previous months, and as the reservoirs of the East London Company were almost empty at the end of September the Company was forced, in October, to use the Lea, without the advantage of the purification resulting from proper storage in the reservoirs. During this critical time we took extra pains to ascertain the character of the East End supply, and additional samples were regularly taken from various points in the district. It is highly satisfactory to report that, in spite of the severe strain thus thrown on their filtering appliances, the clear water supplied to East London has been, bacteriologically, better than it was during the months of August and September.

It has been shown over and over again in these reports that, as a matter of fact, the bacteriological quality of the London water supply does not depend on the use or rejection of flood water, but upon the proper regulation and the efficiency of the filtration. This has long been conducted, substantially, under the supervision of the official Water Examiner appointed under the provisions of the Metropolis Water Act, 1871. The direct use of water from the river during a prolonged flood, depending somewhat on the time of year, may result in the filtered supply containing in solution a little additional vegetable matter, thereby slightly adding to the brown colour, but in our experience during the last fifteen years we have seldom, if ever, known the colour of the London water supply, in its most peaty condition, to equal that of the average colour of Loch Katrine, Thirlmere, or the Welsh Lakes.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

The following are the abstracts of papers received during the vacation and published in the *Transactions*:—

101. "*The Vapour Pressures, Specific Volumes, and Critical Constants of Normal Heptane.*" By Sydney Young, D.Sc., F.R.S.

The critical constants of the specimen of normal heptane obtained by Dr. Thorpe from *Pinus sabiniana* are:—temperature, 266·9°; pressure, 20,415 m.m.; volume of a grm., 4·266 c.c.

A comparison of the ratios of the absolute temperatures (boiling-points) and volumes (liquid and saturated vapour) to the critical constants with those of normal pentane and normal hexane at "corresponding" pressures, shows that, whilst the deviations from constancy are small, the temperature ratios are certainly—and the volume ratios are probably—related to the molecular weights of the paraffins, but a full discussion of this relationship is reserved until the data for normal octane have been obtained.

102. "*Contributions to the Chemistry of Phenol Derivatives.*" By Raphael Meldola and Frederick Henry Streatfeild.

When phenol is brominated in acetic acid solution with one molecular proportion of bromine, and the product afterwards nitrated, a mixture of 4-bromo-2-nitrophenol and 2-bromo-4:6-dinitrophenol is always obtained (*Trans.*, 1896, lxix., 1326). In the present paper the authors show that the bromodinitrophenol is the result of the nitration of both the para- and ortho-bromophenols present in the crude product. The presence of orthobromophenol is proved by the formation of 2-bromo-4-nitrophenol, which the authors have succeeded in isolating from the mixture of nitro-derivatives. The formation of 2-bromo-4:6-dinitrophenol from parabromophenol is not due to "isomeric change" as ordinarily understood, since the first product of the nitration of 4-bromo-2-nitrophenol under the conditions of nitration employed is 4-bromo-2:6 dinitrophenol, and this undergoes isomeric change only when heated with bromine and water (Armstrong, *Trans.*, 1875, xxviii., 520), or nitric acid (Gordon, *Proc.*, 1891, vii., 64), or at ordinary temperatures when the solution in excess of fuming nitric acid is allowed to stand for about two hours. The statement of Hübner and Brenkin (*Ber.*, 1873, vi., 170), that when phenol is brominated in acetic acid and the solid (para) bromophenol frozen out a liquid isomeride in the mother-liquor remains, is thus confirmed. At the same time, the suspicion expressed by Armstrong (*loc. cit.*, 521), that pure parabromophenol gives some "bromo-α dinitrophenol" on nitration, is also confirmed.

The authors have also studied the products of the nitration of pure orthobromophenol. These are 2-bromo-4-nitrophenol (m. p. 112°) and 2-bromo-6-nitrophenol, a new modification (m. p. 67—68°), of which the silver, barium, potassium, and methyl salts are described.

On limited reduction, 4-bromo-2:6-dinitrophenol yields 4-bromo-2-nitro-6-aminophenol (m. p. 141—142°), from which the acetyl derivative (m. p. 161—162), the methyl ether (m. p. 81—82°), and 4-bromo-2:6-dinitraniline were prepared.

The following derivatives of guaiacol were also obtained:—4-bromo-2 nitroguaiacol (m. p. 103—104), 2-bromo-4-nitroguaiacol (m.p. 142°), and acetamidoguaiacol [OH : OMe : NHAc = 1 : 2 : 6], crystallising from water with $1H_2O$, which is lost at 100°.

103. "*Some Iodoso-compounds.*" By John McCrae, Ph.D.

In order to ascertain whether diortho-substituted phenylic iodides yield dichlorides and iodoso-derivatives, the behaviour of orthiododimetadibromotoluene and symmetrical tribromiodobenzene was investigated. The dichlorides were not obtained quite so easily as in the cases of simpler iodides, but this is due to the fact that the iodide dichlorides of these two compounds are more easily soluble in chloroform than the iodides themselves; consequently the dichlorides did not separate until some of the chloroform had evaporated. The dichloride, iodoso-, and iodoxy-derivatives of 5-nitro-2-iodotoluene were also prepared.

104. "*On Myrticolorin, the Yellow Dye Material of Eucalyptus Leaves.*" By Henry G. Smith.

Myrticolorin, $C_{27}H_{28}O_{16}$, exists in large quantity in the leaves of the "red stringy bark," *Eucalyptus macrorhyncha*, and is a new glucoside of quercetin occupying an intermediate position between osyritrin, $C_{27}H_{30}O_{17}$, obtained from the Cape sumach (A. G. Perkin, *Trans.*, 1897, lxxi., 1132), and Viola quercitrin, $C_{27}H_{26}O_{15}$, from the flowers of *Viola tricolor variensis*.

The sugar gave an osazone melting with slight decomposition at 180° when slowly heated, and at 190° with rapid decomposition when rapidly heated. As the osazone of galactose is indicated by these results, and as manna containing sugars is not obtained from the group of Eucalypts to which *E. macrorhyncha* belongs, whilst the principal sugar of the members of the group which do exude manna is raffinose, the question becomes one of importance, and the sugar of myrticolorin will be further examined.

In colour, melting-point, reactions with reagents, and dyeing power, no differences could he detected between myrticolorin and osyritrin, a specimen of which had been forwarded by Mr. A. G. Perkin for comparison.

105. "*Chemical Properties of Concentrated Solutions of certain Salts.* Part II. *Double Potassium Succinates.*" By William Colebrook Reynolds.

The result of the addition of many metallic salts to a concentrated solution of potassium succinate resembles that obtained with a concentrated solution of potassium carbonate (*Trans.*, 1898, lxxiii., 262). Crystalline double succinates, more or less soluble in the solution, were obtained instead of the insoluble metallic succinates in the case of nickel, zinc, cobalt, lead, and calcium.

106. "*Additive Compounds of Organic Bases and Ethereal Salts of Unsaturated Acids.*" By S. Ruhemann and K. C. Browning.

The authors have found that the view expressed by Ruhemann and Hemmy (*Trans.*, 1897, lxxi., 334), with respect to the mode of formation of the compound regarded provisionally as triethylic anhydro-oxalaconitate is correct, as ethylic oxalacetate alone takes part in the reaction. Whilst endeavouring to determine the constitution of that substance, they have observed that piperidine forms additive compounds with ethereal salts of unsaturated acids. These distil in a vacuum without decomposition, have basic properties, and form hydrochlorides which are very soluble in water. The following additive compounds are described: — Ethylic piperidylsuccinate (b. p. 159° at 10 m.m.), ethylic piperidylpyrotartrate (b. p. 163—164° at 10 m.m.), ethylic piperidyltricarballylate (b. p. 201—202° at 10 m.m.), and ethylic piperidylcinnamate (b. p. 220—221° at 11 m.m.

107. "*Formation of Ethereal Salts of β-Ketonic Acids.*" By S. Ruhemann and K. C. Browning.

Adopting Michael's method for the formation of ethereal salts of β ketonic acids by the combination of ethylic sodio-acetoacetate with the ethylic salts of unsaturated acids, the authors have prepared ethylic α-acetotricarballylate (b. p. 187—188° at 11 m.m.), ethylic acetoethyltricarballylate (b. p. 194—196° at 9 m.m.), ethylic α-benzoyltricarballylate (b. p. 244—245° at 10 m.m.), and ethylic α-acetobutanetetracarboxylate (b. p. 222—223° at 10 m.m.),

108. "*Disulphonic Acids of Toluene, of Ortho- and Para-toluidine, and of Ortho- and Para-chlorotoluene.* By William Palmer Wynne, D.Sc., F.R.S., and James Bruce, B.Sc.

The authors correct certain errors which occur in their previous communication (*Proc.*, 1895, xi., 153), and show that the para-toluidinedisulphonic acids obtained by Richter from the 1:4:3- and 1:4:2-para-toluidinesulphonic acids (*Annalen*, 1885, ccxxx., 314, 331) are the 1:4:3:5- and 1:4:2:5-derivatives respectively. They also show that the toluene disulphonic acid previously described as the 1:2:6-derivative is the 1:2:5 compound.

Paratoluidine-3:5- and 2:5-disulphonic acids, and orthotoluidine 3:5- and 4:5-disulphonic acids, together with the corresponding chloro-acids, are described, and the statements of Hasse (*Annalen*, 1885, ccxxx., 286) with respect to the bromotoluenedisulphonic and toluenedisulphonic acids derived from orthotoluidine-3:5-disulphonic acid are shown to be erroneous.

Parachlorotoluene-3- and -2-sulphonic acids, and orthochlorotoluene-4-sulphonic acid, together with the disulphonic acids derived from them by further sulphonation are described, and the conclusion is drawn that the mixture of monosulphonic acids obtained on sulphonating parachlorotoluene contains not more than 14 per cent of the 1:4:3-isomeride.

Incidentally, the list of six toluenedisulphonic acids given by Klason (*Ber.*, 1887, xx., 350) has been revised, and it is shown that only five of the six acids theoretically possible are known. Experiments are in progress with the object of obtaining the missing 1:2:3-isomeride.

109. "*Chlorine Derivatives of Pyridine.* Part II. *Interaction of Ammonia and Pentachloropyridine. Constitution of Glutazin.* By W. T. Sell, M.A., and F. W. Dootson, M.A.

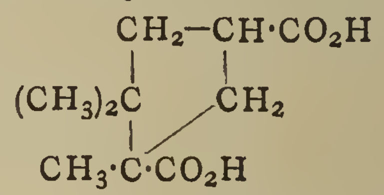
The authors describe the preparation from pentachloropyridine of γ-amidotetrachoropyridine, (presumably α-) amidotetrachloropyridine, diamidotrichloropyridine, and hydroxytetrachloropyridine. γ-Amidotetrachloropyridine is identical with the compound obtained by Stokes and Pechmann (*Ber.*, 1887, xx., 2655) from glutazin, and thus demonstrates the presence of an amido-group in the latter substance.

110. "*Mercury Acetamide.*" By M. O. Forster, Ph.D., B.Sc.

Mercury acetamide liberates nitrogen from hydroxylamine, hydroxylamine hydrochloride, hydrazine, hydrazine hydrochloride, and phenylhydrazin, being resolved by these substances into acetamide and mercury, which, in the case of the salts mentioned, are accompanied by calomel; the products from phenylhydrazin are aniline, benzene, and mercury diphenyl. Phenylhydroxylamine is converted into nitrosobenzene and azoxybenzene by the agency of mercury acetamide, which transforms hydrazobenzene into azobenzene. Nitrosophenylhydroxylamine, aniline, and diazoamidobenzene yield additive compounds with mercury acetamide.

111. "*Sulphocamphylic Acid and Isolauronolic Acid, with Remarks on the Constitution of Camphor and some of its Derivatives.*" By W. H. Perkin, jun.

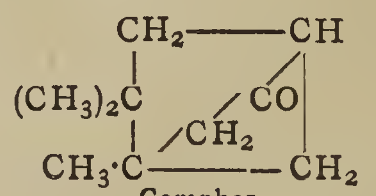
In this communication the author shows that the results which he and others have obtained in the investigation of isolauronolic acid can, apparently, be explained only on the assumption that camphoric acid has the formula—



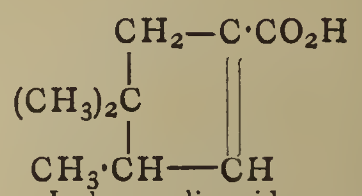
With the aid of this formula, the oxidation of isolauronolic acid, $C_9H_{14}O_2$, to isolauronic acid, $C_9H_{12}O_3$, and further to γ-acetyldimethylbutyric acid,—

$$CH_3{\cdot}CO{\cdot}C(CH_3)_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H,$$

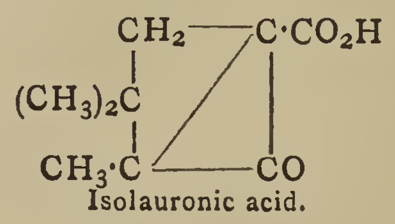
is readily understood. Assuming that the above constitution for camphoric acid is correct, the author deduces the following formulæ as probably representing the constitution of some of the more important members of the camphor group:—



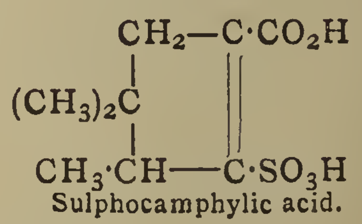
Camphor.



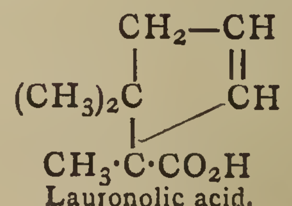
Isolauronolic acid.



Isolauronic acid.



Sulphocamphylic acid.



Lauronolic acid.

These formulæ are shown to explain the properties of the substances in a satisfactory manner.

112. "*Researches on the Terpenes. VIII. On Carvenol: its Reactions and Products.*" By J. E. Marsh and A. Hartridge.

Carvenol, the product of the action of strong sulphuric acid on chlorocamphene, and previously described as hydroxycamphene or camphenol (*Trans.*, 1897, lxxi., 290), has been further examined. It has been found to yield chlorocymene [Me : Cl : Prβ = 1 : 2 : 4] by the action of phosphorus pentachloride, and paracymene by the action of benzoic chloride. It is reduced by sodium in alcoholic solution, forming the secondary alcohol *carvanol*, $C_{10}H_{20}O$, which is hexahydrocarvacrol. This latter compound yields, on oxidation, the saturated ketone *carvanone*, $C_{10}H_{18}O$.

The production from camphor of cymene and chlorocymene by comparatively simple reactions, and also of reduced cymene derivatives, brings into prominence the close relationship which must exist between camphor and cymene. Not only do formulæ which fail to express this relationship in the arrangement of the carbon atoms lose the chief support on which any formula for camphor must rely, but, further, in view of the production of chlorocamphene, a saturated compound, no formula can be admitted which leads to the representation of camphene and chlorocamphene as unsaturated compounds.

113. "*Optically Active Alkyloxypropionic Acids.*" By Thomas Purdie, F.R.S., and G. Druce Lander, B.Sc.

As the product of the action of isopropylic iodide on inactive silver lactate contains a considerable quantity of isopropylic isopropoxypropionate (*Trans.*, 1898, lxxiii., 296) the authors concluded that the abnormally high rotation of the active ethereal lactates prepared by the silver salt method (*Trans.*, 1895, lxvii., 916; 1896, lxix., 830) was due to their contamination with small quantities of active ethereal alkyloxypropionates. If this conclusion is correct, the alkyloxypropionic acids must be substances of very high optical activity. With the view of verifying this, the active α-methoxy, ethoxy, and propoxy-propionic acids have been prepared.

As complete racemisation occurs during the action of sodium ethylate on active ethylic chloro- and bromopropionates (*Trans.*, 1896, lxix., 819), the active alkyloxy-acids were prepared by the re-solution of the inactive acids with alkaloids. The re-solution of ethoxypropionic acid was carried out with cinchonidine, and more completely with morphine, the salt of the dextro-acid being in both cases the less soluble. The methoxy- and propoxy-acids were also resolved with both alkaloids, but the re-solution with cinchonidine was far from complete. In the case of the methoxy-acid, both alkaloids precipitate first the lævo-acid; in the case of the propoxy-acid, the cinchonidine salt of the lævo- snd morphine salt of the dextro-acid are first deposited. The authors point out that the results of their experiments are not in harmony with the theory of Winther (*Ber.*, 1895, xxviii., 3000).

Polarimetric observations were made on the *l*-methoxy-, *d*-ethoxy-, and *d* propoxy-acids, and on their sodium and calcium salts, also on barium and silver *d*-ethoxypropionates. The substitution of the alcoholic hydrogen of the lactates by an alkyl-group produces, as was expected, a great increase of optical activity. Thus the molecular rotation of the alkaline lactates in dilute aqueous solution is 14·5°, while that of sodium ethoxypropionate is 68·77°. Increase in the weight of the introduced alkyl group produces a very much smaller but still distinct rise of molecular rotation. The rotations of the salts increase with dilution, and in general conform to the law of Oudemans and Landolt; those of the acids diminish. The changes of rotation with varying concentration are, as might be expected from the disappearance of the hydroxyl group, of a more normal kind than in the case of lactic acid and the lactates, but the authors conclude that even in the case of the alkyloxy-acids, the rotation is influenced by other factors connected with the solvent besides electrolytic dissociation.

114. "*The Optical Activity of Gallotannic Acid.*" By Otto Rosenheim, Ph.D., and Philip Schidrowitz, Ph.D.

The authors have examined a number of commercial "pure" gallotannic acids, and find that, whilst they varied in optical activity from $[\alpha]_D + 11°$ to $[\alpha]_D + 74·2°$, they all contain from 50 to 75 per cent of a uniform gallo-tannic acid possessing an optical activity of approximately $[\alpha]_D + 75°$. The authors ascribe this great difference to the fact that the commercial substances contain varying quantities of gallic acid, which is inactive, and mineral matter, which possesses a great influence on rotatory power. Acetyl derivatives and quinine salts prepared from the commercial samples are respectively identical in optical activity among themselves and with the products obtained from the homogeneous substance isolated by the author's method.

115. "*The Influences Modifying the Specific Rotatory Power of Gallotannic Acid.*" By Otto Rosenheim, Ph.D., and Philip Schidrowitz, Ph.D.

The authors have examined the modifying influence of—(*a*) concentration, (*b*) nature of the solvent, and (*c*) optically inactive substances, on the specific rotation of gallotannic acid. The material used for these experiments was the homogeneous product obtained by methods described in the preceding paper. The results were as follows:—

(*a*). *Concentration.*—In aqueous solutions containing not more than 1 per cent, the rotation is constant at $[\alpha]_D\ 15 + 75·2°$. From 1 to 10 per cent, the rotation decreases gradually to $[\alpha]_D\ 15 + 66·1°$.

(*b*). *Nature of the Solvent.*—The optical activity of gallotannic acid depends to a very marked extent on the nature of the solvent. Thus, the original specific rotation $[\alpha]_D\ 15 + 75·2°$ (for water) is reduced to $\pm 0°$ for a mixture of acetone and carbon tetrachloride. Alcohol, ethylic acetate, &c., and mixtures of acetone with ether, &c., have a powerful depressing action, and the gross effect produced is greater in the case of gallotannic acid than in that of any other substance hitherto examined.

(*c*). *Influence of Optically Inactive Substances.*—1. *Acids:* Mineral acids have no influence. Acetic acid has a depressing effect, but this is probably due to partial acetylation. Gallic acid has no influence. 2. *Ammonia:* A few drops added to a 1 per cent solution produce total inactivity. 3. *Salts:* Salts, such as sodium tungstate, sodium, potassium, ammonium, and lithium biborates and chlorides, sodium and potassium bicarbonates, and zinc acetate, exercise a very marked influence on the rotation of gallotannic acid. In the majority of cases, the addition of increasing amounts of salt produces a decrease in the specific rotation until a minimum is attained, the further addition of salt causing a gradual rise. The molecular rotations of the mixtures at the minima are approximately constant and equal to the molecular rotation of gallotannic acid alone.

116. "*The Non-resolution of Racemic Tetrahydropapaverine by Tartaric Acid.*" By William Jackson Pope and Stanley John Peachey.

Prior to the publication of Goldschmiedt's paper (*Monats.*, 1898, xix., 321), the authors had prepared the dextrotartrate of racemic tetrahydropapaverine in the course of their work on the re-solution of the base into its optically active components (*Proc.*, 1898, xiv., 122). The salt has the composition assigned to it by Goldschmiedt, and belongs to the monosymmetric system; $a : b : c = 1·1464 : 1 : 0·7932$; $\beta = 82°\ 30'$. Its molecular rotation was found to be $[M]_D = +63·44°$, a value agreeing with those obtained for the metallic tartrates in dilute aqueous solution, namely, 58·1 to 64·6 (Landolt, *Ber.*, 1873, vi., 1077).

Ladenburg has described as "hemiracemic," salts in which either the acid or the base is racemic whilst the other constituent is optically active, and has examined two salts of the kind, namely, quinine racemic pyrotartrate

(*Ber.*, 1898, xxxi., 524, 937) and strychnine racemate (*Ber.*, 1898, xxxi., 1969). Racemic tetrahydropapaverine dextrotartrate is thus the first case of the kind in which a racemic base is combined with an optically active acid.

PHYSICAL SOCIETY.

Ordinary Meeting, November 11th, 1898.

Mr. Shelford Bidwell, F.R.S., President, in the Chair.

The discussion on Mr. Albert Campbell's paper on "*The Magnetic Fluxes in Meters and other Electrical Instruments*" was resumed.

Prof. Ayrton said he wished to offer some remarks on behalf of Mr. Mather and himself. The paper would perhaps have received more adequate discussion at the Institution of Electrical Engineers, for it was chiefly of a technical character. The importance of neutralising the effect of leads when using instruments with very weak fields, such as Siemens's electro-dynamometer, should be emphasised. In instruments of the Kelvin-balance type, where two opposed coils carry two opposed currents, the field spreads at the edges; the true "working" flux is not that directly between the coils. Mr. Campbell would have done better if he had used a long search-coil wound round one of the swinging coils, forming part of a vertical cylinder. It would have been well also to have supplied some experimental proof that the astatic arrangement of the swinging coils of the Kelvin balance makes the instrument independent of the earth's field. The effect of the earth's field is of the order 0·2, so that with instruments of the Weston type, with a field of the order 1000, it was sometimes assumed, erroneously, that the readings were practically independent of the earth's H. Prof. Ayrton's own tests showed that by turning a Weston voltmeter towards different points of the compass, the errors in a particular case were far greater than might be predicted from the above ratio; the induction in the voltmeter pole-space, due to the earth's field, was much higher than 0·2; the earth's field was exaggerated by the iron pole-pieces; it was not necessary to suppose that the magnetism of the permanent magnet caused the variation. The error observed was about 0·2 per cent in a horizontal field, and 0·8 per cent when the field of the voltmeter was parallel to the earth's induction. Here the induction in the gap was 1200, and H = 0·2. In tests relating to the Ayrton and Perry magnifying-spring voltmeter, it was more important to know the B in the air-space *near* the iron than the B *within* the iron. Eddy currents might account for the extraordinary results obtained in the Shallenberger meter.

Mr. J. H. Reeves described a method he had adopted for measuring the effect of stray fields upon ammeters and voltmeters. The instrument to be tested is first mounted on a stand, and is brought under the influence of a large coil carrying a current. In this way fields of known magnitude can be superimposed on the working field throughout the range of the instrument, and the change of deflection due to them can be observed. From these known values the working field can be deduced. For let the current in the solenoid of the instrument at any moment be A ampères, producing a corresponding unknown working field of magnetic force X. Then X is proportional to the solenoid current, as measured by the indications of the instrument. If a magnetic force x is superimposed on X, then x is measured by x/X of A. If x is known, the working field X can be calculated from the change of deflection produced by the superposition. With Evershed ammeters the field measured in this way was in one instrument 200, and in another 226; or about one-third of Mr. Campbell's figure (700) for the Evershed ammeter. Mr. Campbell's value of B did not represent the working field, but the field at the end of one of the fixed pieces of iron.

Mr. Campbell, in reply, said he thought the theory of electrical instruments to be well within the limits of Physics, and he had for that reason presented the paper to the Physical Society. The position chosen for the search coil in the Kelvin-balance tests may not have corresponded to the working flux, but it was near to the right position, and he had carefully specified the position chosen. His results as regards the Weston instrument differed from those of Prof. Ayrton; the errors he had observed for the particular ammeter used were under 0·1 per cent. The earth's field probably produced an effect different for different Weston instruments, according to the degree of saturation of the permanent magnet. In Mr. Campbell's tests the Weston instrument did not have an iron case.

A paper by Prof. W. B. Morton, on "*The Propagation of Damped Electrical Oscillations along Parallel Wires,*" was then read by Prof. J. D. Everett.

In a paper published in the *Phil. Mag.* for September, 1898, Dr. E. H. Barton compared the attenuation of electrical waves in their passage along parallel wires, as experimentally determined by him, with the formula given by Mr. Heaviside in his theory of long waves. He finds close agreement as regards the effect of a terminal resistance, but large discrepancy in the case of the attenuation-constant. Prof. Morton now investigates how far the results should be modified when it is supposed, as under actual conditions, that the oscillations propagated from the origin are damped, and that the circuit is not balanced, as in the ideal case of distortionless transmission. He finds (1) that the velocity of propagation is increased, while (2) the attenuation is increased, and (3) with infinite resistance between the ends of the wires, the waves are, as before, reflected completely with phase unchanged. As the resistance is diminished the amplitude of the reflected waves is decreased, and a phase-difference is introduced. For a certain value of the resistance the reflected amplitude is a minimum, and the phase-difference is $\pi/2$. When the resistance is zero, there is again complete reflection, with phase-difference π; *i.e.*, the waves are reversed. The result is that the reflection-factor for amplitude *seems* to pass continuously from $(+1)$ to (-1) *without* passing through zero. Using the numbers given by Dr. Barton it is found that the corrections to the simple theory are extremely small, so that in actual cases the damping may be ignored, and the circuit may be regarded as distortionless.

Mr. Oliver Heaviside (abstract of communication).—Mr. Heaviside, using his own notation, exhibits mathematically the connection between the case investigated by Mr. Morton, of a wave-train arising from a damped source, and the standard case of an undamped source. The cause of the attenuating coefficient coming out twice as great in Dr. Barton's experimental conditions as when the resistance is calculated by Lord Rayleigh's formula, is attributed to lack of correspondence between the experimental conditions and those of the ideal theory. For—(1) The external resistance, of unknown amount, is ignored. (2) It is not certainly to be expected that the formula in question is true for millions of vibrations per second. It may, however, be concluded from the experiments that the theory furnishes an approximation to the real resistance. (3) The magnetic vibrations to which the wires are subjected are not long-continued and undamped, as assumed by the formula. When a wave train passes any point on a wire its surface is subjected to an impulsion vibration lasting only a very minute fraction of a second; a vibration, moreover, which is very rapidly damped. So there is no definite resistance, and the resistance is greater than according to Lord Rayleigh's formula. (4) Perhaps, also, the terminal reflections involved in Dr. Barton's calculations may introduce error.

The President proposed votes of thanks to the author, and the meeting was adjourned until Nov. 25th.

NOTICES OF BOOKS.

Twenty-second Annual Report of Her Majesty's Inspectors of Explosives. Being their Annual Report for the Year 1897. London: Eyre and Spottiswoode. Edinburgh and Glasgow: John Menzies and Co. Dublin: Hodges, Figgis, and Co. 1898. Pp. 208.

The report of Her Majesty's Inspectors of Explosives shows in a very emphatic manner what minute but rigorous precautions are taken to guard against accidents in the manufacture and handling of the enormous and ever-growing trade in high explosives. Accidents accompanied by death or maiming are comparatively rare, thanks to the vigilance of the inspectors.

There has been no further modification in the law during the year; but an Order in Council (No. 17) has been made under Section 104 of the Act placing acetylene when in the liquid state, or subject to a certain pressure, on the list of explosives within the meaning of the Act.

The number of factories has decreased by one, but three new ones have been added since 1896, while ten applications for new licences are still under consideration. The four extinct factories were either practically not in use or have been superseded by new ones. Every factory and magazine has been visited at least once, and many of them twice, during the year.

The number of deaths from accident has been only nine, and although above the ten years' average (5·2), it is, as we pointed out above, relatively inconsiderable.

Eight new explosives have been added to the authorised list, full definitions of which will be found in Appendix D (1). Out of 321 samples of explosives examined during the year, only 26 were rejected.

There has, we are glad to see, been no falling off in the general improvement referred to in the last report. A very high standard of excellence was reached soon after the passing of the Act in 1871, and this has been fully maintained during the past year; in fact, in only one case was it found necessary to take proceedings, and in only three cases explosives were placed under seizure.

The total number of magazines is now 390, being an increase of six over last year, and it is satisfactory to note that there has been no case of unlawful entry into either a magazine or factory during the year, neither has there been any case of fire or explosion in any of the 390 magazines during the same period.

There is a decrease in the quantity of foreign nitroglycerin compounds imported during the year. In 1896 the amount imported was 1,259,200 lbs., and in 1897 it had fallen to 1,153,550 lbs. The amount of carbonite has fallen off, and gelatin dynamite again heads the list.

In the special section on accidents are to be found tables giving not only the few which have occurred at factories, but also many others in different parts of the country, due to carelessness or else unexplained. We note that in the last ten years there have been only 14 deaths due to explosions of gunpowder. Following the practice of former years, a brief account of the more interesting foreign explosions is also given. On September the 8th some dynamite exploded at the George Goch mine, Johannesburg, killing 8 natives and wounding 12 others; and in April two cases of blasting gelatin exploded in the 1250 foot level of the Langlaagte Deep, Johannesburg, by which 8 white men and 26 natives lost their lives. The explosion shook the whole of the upper levels. At San Salvador, in America, a dynamite explosion occurred by which two blocks of buildings were destroyed and a number of persons killed. There were also several serious explosions of fireworks reported by which many people were killed and injured in different parts of America. At Cumpas, in Mexico, 3 tons of blasting powder blew up, killing 20 people and injuring others, while nearly every building in the town was injured. A terrible explosion took place at Rustchuk on the 6th of August, by which 200 people were killed. Several million old army cartridges were being emptied in one large shed in which over 300 persons were employed; it is supposed that a cartridge was dropped, but the wonder is that anyone escaped. There are many others of more or less magnitude in the list, but it would be tedious and unprofitable to go through them. Thanks, however, to the thorough and excellent system of storage, isolation, and inspection adopted in England, we are practically free from such terrible catastrophies we so often hear of from abroad.

Pharmaceutical Formulas: a Book of Useful Recipes for the Drug Trade. Second Edition. By Peter MacEwan, F.C.S. London: Office of the *Chemist and Druggist.* 1898. Pp. 664.

The rapidity with which this edition has followed the first, which was published only one month previously, shows that there was a great demand for such a book. The task of collecting and collating the very large number of formulas has been a formidable one. A large proportion of them had to be proved, and the results of these provings are partly embodied in the book. The formulas have been taken principally from *The Chemist and Druggist* and "The Chemist's and Druggist's Diaries," and include such various matters as toilet preparations, hair washes, dentifrices, beverages, antiseptics, disinfectants, inks, varnishes, medicinal compounds, &c.

The customary signs employed in prescriptions are as a rule used in the formulas, and the British rule "solids by weight, liquids by measure," applies throughout unless otherwise stated. An Addenda informs the reader that, owing to the publication of the British Pharmacopœia, 1898, a certain number of formulas (the list is given in full) should be compared with those in the Pharmacopœia and the changes noted.

There is no doubt but that this book will be of great value to druggists and pharmaceutical chemists, and will cause them a great saving of time. We are glad to see that there is an excellent index of 25 pages, enabling any formula to be found almost immediately.

Elementary Physics, Practical and Theoretical. First Year's Course. By John J. Kerr, M.A. London: Blackie and Sons, Lim. 1898. Pp. 140.

This book is divided into two principal parts, viz., Laboratory Work, from page 1 to page 63; and Classroom or Theoretical Work, from page 64 to 140. These chapters, seventeen of each, correspond and should be read together. They begin with the measurement of length, the vernier and screw gauge are then described, after which we have the methods of measurement of area, volume, mass, time, and force, accompanied by descriptions of, and the manner of using, the spring balance, the beam balance, and the pendulum. The next few chapters deal with the parallelogram of forces, the inclined plane, movements, centre of gravity, &c., and the final ones explain the principle of Archimedes, the pressure due to liquid columns, the hydrometer, and Boyle's law. It is essentially a book for beginners, and is well arranged; everything is clearly and thoroughly explained both in the practical and theoretical parts, and should be of great help to young students.

The Rare Earths; their Mineralogy, Properties, and Analysis. ("Les Terres Rares; Minéralogie, Propriétés, Analyse"). By P. Truchot. Paris: Georges Carré and C. Naud. 315 pages. Price 5 francs.

This work puts on record our present knowledge of the physical and chemical properties of the rare earths. The application of some of the earths of this group to the purposes of lighting have brought them into notice, and have given rise to a large amount of chemical literature. The work is divided into three parts.

1. *The Mineralogical Part* contains a valuable table of all the rare earth minerals; a detailed study of the principal minerals, especially the monazite sands, now almost exclusively employed in the manufacture of incandescent mantles; and a review of the geographical distribution of the chief deposits of these minerals, illustrated with maps.

2. *The General Part* contains a description of the rare elements and their organic and inorganic salts.

3. *The Analytical Part* comprises much that is known in France on the different methods of fractionation and separation, the analytical characters of the different rare earths, and the methods of analysis of commercial products, such as nitrate of thoria, precipitated thoria, monazite sands, incandescent mantles, &c.

This book will be useful to all who take an interest in the chemistry of the rare earths or who are engaged in the development of the important industries to which they have largely contributed. At the same time it has the great faults of so many otherwise excellent French books; it has no index, and it is written from a purely French point of view, little or no mention being made of the work done by Englishmen on the fractionation of the rare earths and in so many other directions.

A History of Chemistry from the Earliest Times to the Present Day; being also an Introduction to the Study of the Science. By Ernst von Meyer, Ph.D., Professor of Chemistry in the Technical High School, Dresden. Translated, with the Author's Sanction, by George McGowan, Ph.D. Second English Edition, translated from the Second German Edition, with numerous Additions and Alterations. London: Macmillan and Co., Lim. New York: The Macmillan Company. 1898.

It is a great satisfaction to find that we have already a translation of the second edition of this well known and interesting work. Since the first edition, in 1891, many valuable sources of information have become available and have enabled the author to add much new matter in the earlier chapters of the book, while the many great advances that have been made in chemistry since that date have been followed up and included. Although professedly a translation of the second German edition of 1895, it has been brought quite up to date by additions both by the author and the translator with the author's sanction and approval. It has thus been possible even to include an account of the recent researches on the complex nature of the atmosphere by Rayleigh, Ramsay, and others.

We have little doubt that the appreciation that has been shown by English readers for the first edition will be extended also to this.

CORRESPONDENCE.

ESTIMATION OF SULPHUR IN COALS, COKES, AND ORES.

To the Editor of the Chemical News.

Sir,—Objection has been taken to our method of estimating sulphur (roasting with sodium carbonate, solution in water, filtering, acidulating filtrate with HCl, and precipitating by barium chloride, *vide Journ. Soc. Chem. Ind.*, March 29, 1886; *Journ. Iron and Steel Inst.*, 1896, No. 2) on the ground that silica from the ash, or gangue, entering into solution will be precipitated together with the barium sulphate. To our minds, this objection was met by the close agreement between the results obtained by our method and by the aqua regia method in the analysis of iron ores; but to put the matter to the test, we have examined the precipitates of $BaSO_4$ in varying experiments and have failed to detect the presence of silica in a single instance.

We find that some silica is dissolved by the water, but when the heat has not been so intense as partially to fuse the mixture, the amount dissolved is only small. But whether small or large, the barium sulphate is precipitated free from silica.—We are, &c.

R. W. Atkinson.
Alex. J. Atkinson.

Laboratory and Assay Office,
14, Loudoun Square, Cardiff, Nov. 11, 1898.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvi., No. 2, July 11, 1898.

Decomposition of Nitric Acid by Heat at Low Temperatures.—M. Berthelot.—When nitric acid was sealed up in a tube from which the air had been pumped out, and left in darkness for two months, no gas was formed if the tube was kept at the ordinary temperature of the laboratory; when kept in darkness at 100° it slowly decomposed, forming peroxide of nitrogen, oxygen, and water:—$2HNO_3 = 2NO_2 + O + H_2O$. The decomposition remained incomplete and could never become total owing to the formation of water. This water forms hydrates of nitric acid, which are much more stable than the pure acid. A limit was reached, and this was determined for a low temperature. If there is an inverse reaction produced at all in the cold it is excessively slow.

The Form of Oxidation of Cobalt Salts in Alkaline Solution.—André Job.—When a solution of a salt of cobalt is added drop by drop to a solution of bicarbonate of potassium a clear rose-coloured liquid is produced. A small quantity of peroxide of hydrogen or bromine water added to this turns the colour to green. Many attempts have been made to separate and analyse the green compound. The author obtains satisfactory results by employing ferrous solutions, which when added to the green cobalt solution change the green colour to rose. A known quantity of cobalt is peroxidised, and to it is added a known quantity of ferrous pyrophosphate; the excess of the latter is estimated by iodine. The numbers found agree with the oxidation formula, $2CoO + O = Co_2O_3$. The chief difficulty is to insure the complete peroxidation of the cobalt: to do this a large excess of hydrogen peroxide is added to the alkaline cobalt salt and left for several days. From this reaction a rapid and easy method of estimating cobalt in the presence of nickel and iron may be deduced; for nickel is not oxidised under these conditions, and ferric salts are not reduced by ferrous pyrophosphate.

Mixed Carbonic Esters of Phenols and Alcohols.—P. Cazeneuve and A. Morel.—By means of the general method of preparing mixed carbonic esters of the fatty and aromatic series, described by the authors in the preceding issue, mixed carbonates have been prepared of ordinary phenol and methyl, ethyl propyl, isopropyl, isobutyl, isoamyl, and allyl alcohols respectively. These esters have all been obtained by boiling phenyl carbonate with the different alcohols in presence of pyridine or urea. A description of their preparation and properties is given. It is remarked that the series thus obtained presents anomalies in certain physical properties which are unexplained at present. The boiling-points do not increase with the molecular weights, which, however, is the rule for esters of the same homologous series. With these mixed carbonic esters the boiling-point varies slightly for the different esters, under reduced as well as under normal pressure, being about 220° at normal pressure and about 120° at a pressure of 30 m.m. Again, the density at zero of these esters, instead of increasing decreases from phenyl-methyl carbonate to phenyl-methyl-amyl carbonate.

Action of Heat on the Double Nitrites of the Metals of the Platinum Group. Rhodium Compounds.—A. Joly and E. Leidié.—The double nitrites which rhodium forms with potassium, sodium, and barium decompose under the influence of heat, giving salts comparable with those of ruthenium and iridium. The decomposition starts at 360°, but is quickest at 440°. The analysis of the decomposition products at this temperature shows the existence of RhO_2, which had been suspected by Claus, who hesitated whether to give it the formula RhO_2 or $RhO.RhO_3$. The decomposition reaction is probably represented by one of the two equations :—

$$3[Rh_2(NO_2)_{12}K_6] = \\ = (6RhO_2K_2O) + 6NO_2K + 10NO_3K + 3N + 17NO,$$

or—

$$3[Rh_2(NO_2)_{12}K_6] = \\ = (6RhO_2K_2O) + 4NO_2K + 12NO_3K + 5N + 15NO.$$

The Yttria Earths found in Monazite Sands.—G. Urbain.—Already inserted in full.

Bromination by means of Aluminium Bromide in the Fatty Series.—A. Mouneyrat.—In a previous paper the author has described the power of aluminium chloride to produce compounds containing double bonds with chlorhydrocarbons of the fatty series. He now finds that aluminium bromide has a similar effect upon brominated hydrocarbons. The following proof is given :—Anhydrous ethylene dibromide ($CH_2Br.CH_2Br$) is heated to 100—110° over a paraffin bath with anhydrous $AlBr_3$. Hydrobromic acid is copiously evolved and a gas which proves to be acetylene. The reaction probably occurs thus :—

$$(1)\ CH_2Br - CH_2Br + 2AlBr_3 = \\ = AlBr_2 - CHBr - CHBr - AlBr_2 + 2HBr.$$

$$(2)\ AlBr_2 - CHBr - CHBr - AlBr_2 = 2AlBr_3 + CH \equiv CH\cdot$$

The supposition now is that bromination can be effected by means of aluminium bromide. The brominating action of $AlBr_3$ upon ethyl bromide ($CH_3—CH_2Br$) was investigated. A solution of $AlBr_3$ in anhydrous bromine was used, and the compounds ethylene dibromide ($CH_2Br—CH_2Br$), acetylene tetrabromide ($CHBr_2—CHBr_2$), and hexabromethane ($CBr_3—CBr_3$) successively obtained. The formation of the latter compound is explained by the following equations :—

$$(1)\ CHBr_2 - CHBr_2 + 2AlBr_3 = \\ = AlBr_2 - CBr_2 - CBr_2 - AlBr_2 + 2HBr.$$

$$(2)\ AlBr_2 - CBr_2 - CBr_2 - AlBr_2 + 4Br = \\ = CBr_3 - CBr_3 + 2AlBr_3.$$

Hence we have a simple method of replacing in successive stages all the hydrogen atoms of ethane by bromine.

Action of Chlorides of Tetrazodiphenyl, Tetrazo-di-ortho-tolyl, Tetrazo-di-ortho-anisyl on the Cyanacetates of Methyl and Ethyl.—G. Favrel.—Not suitable for abstraction.

Rate of Saponification of the Esters of Phosphoric Acid.—J. Cavalier.—In order to compare, from the point of view of stability, the three phosphoric esters of any one alcohol, their rates of saponification by water are measured, the conditions of temperature and concentration being the same for each. On warming an aqueous solution of a neutral phosphoric ester, R_3PO_4, a mixture is obtained of the original ester and the three acids HR_2PO_4, H_2RPO_4, and H_3PO_4. Curves can be plotted representing, as a function of the time, the quantities of the different acids produced by decomposition of one molecule of the neutral ester, and the rates of decomposition of the three esters calculated. Results are given of a study of the three methyl esters and ethyl esters, and the two acid allyl esters. The methyl esters decompose more rapidly than the corresponding ethyl esters.

Journal de Pharmacie et de Chimie, vol. vii., No. 11.

The Estimation of Theobromine.—M. François.—The reactions of theobromine, like those of caffein based on oxidation, being difficult to recognise, the author gives two or three tests, with minute instructions as to their proper carrying out, and also the quantities to use. The test for purity is based on the very slight solubility of theobromine in strong alcohol, the most probable adulterant being caffein; the author has calculated the exact degree of solubility of both these substances in alcohol at 95 per cent, at a temperature of 21°. In testing for identity he dissolves 0·1 grm. of theobromine in a warm mixture of 1 part of nitric acid to 2 parts of water, then adds 10 c.c. of nitrate of silver at 10 per cent. A cloudiness is caused; the solution must be heated until it is clear on cooling; colourless needles are deposited. Another method is to use hydrochloric acid, and then add 10 c.c. of saturated bromine water; after heating to drive off the excess of bromine, the flask and its contents must be brought up to their original weight with distilled water. The cooled liquid stains the skin red. In determining the relative solubilities of theobromine and caffein the following constants were found :—10 c.c. of alcohol at 95°, saturated with theobromine at a temperature of 21°, contained 0·0045 grm. in solution, and under the same conditions 0·0930 grm. of caffein was contained in solution: from these data it is easy to calculate the amount of adulteration by caffein.

Note on Croton Oil.—M. Javillier.—Croton oil prepared by simple pressure, by lixiviation with ether at 0·758, or by double digestion at 75° in alcohol at 95° has different appearances, and gives different results on analysis, and also different returns; the first gave 12·5 per cent, the second 38 per cent, and the third 12 per cent. If 1 volume of the first oil be heated with 2 volumes of absolute alcohol, there is complete solution at 75°, but on cooling 0·8 per cent in volume of the oil separates; the second oil acts in the same manner, while the third is entirely soluble even in the cold. The first two oils congeal at −7° and the third at −8°, but they all commence to thicken before reaching zero. The index of iodine absorbed by these oils for 100 c.c. of each is—No. 1 = 109, No. 2 = 108, No. 3 = 91·2. Commercial oil generally has an index equal to 102. The index of saponification was found to be—No. 1 = 192·9, No. 2 = 194·5, No. 3 = 260·6, and commercial oil 205·6. The index of acidity was—No. 1 = 27·3, No. 2 = 30·9, No. 3 = 60·1. To sum up, it appears that the oil extracted by alcohol (No. 3) differs considerably from the other two, which are almost identical.

On the Acid Phosphoglycerates.—MM. Adrian and Trillat.—When we add to an aqueous solution of a glycerophosphate of baryta a little dilute sulphuric acid, a sulphate of baryta is formed, while the liquid remains neutral to heliantine; the precipitate continues to form until there is just an excess of acid. This reaction does not give free phosphoglyceric acid, but an acid salt; if this salt is treated with a soluble sulphate a double decomposition takes place. These two reactions show that it is possible to obtain acid glycerophosphates by two methods:—1st, by the decomposition of a neutral glycerophosphate by sulphuric acid; and 2nd, by double decomposition between an acid glycerophosphate and a soluble sulphate. The preparation of the acid salts of barium, zinc, and magnesia are then described, and the results of their analyses given. When an acid glycerophosphate is dried at 130° it appears to be anhydrous, but when powdered it is extremely hygrometric. The principal difference between these last and the neutral salts is their great solubility in cold water, as well as in water to which alcohol has been added. They are not sensibly decomposed by heat; they are distinguished from the neutral and acid phosphates by the same reactions as the neutral glycerophosphates; acetate of lead gives a white precipitate soluble in acetic acid; but neither molybdate of ammonia, acetate of uranium, nitrate of silver, or ferric chloride, give any precipitate at all.

MISCELLANEOUS.

The Countess of Warwick's Secondary and Technical School at Bigods, Dunmow, Essex.—We are pleased to learn, by the report of an Address delivered at the above Institution by Professor Raphael Meldola, F.R.S., that an attempt is being made to introduce scientific training into the rural districts. The wisdom of such a movement must be apparent to every one, and we can heartily commend the philanthropy and foresight of the lady to whom this first experiment is due. That a need exists in this direction is at last becoming recognised, and we hope that the experiment in Essex may meet with all the success it deserves, and lead to similar movements in other districts. No doubt difficulties will be met with at first, and possibly a good deal of indifference and want of appreciation from the very class whom it is desired to benefit; but difficulties can be overcome, and those who have the cause at heart will look rather to future results than present appreciation. We should not wonder if it is found that the *material* turns out to be of even better quality than the authors of the movement expect, for we cannot forget that among our greatest men there are many whose early years were spent far from the great centres of learning, and there are unquestionably many instances where true talent has either lain dormant or has developed abnormally for want of a little scientific training. We are really glad to find at least one attempt to replace by systematic scientific education the occasional spasmodic "lecture," that in many instances only tends to "amaze the unlearned," and we shall watch with interest the development of the movement.

Action of Arseniuretted Hydrogen on Mercuric Chloride.—A. Partheil and E. Amort.—When arseniuretted hydrogen is passed into an acoholic solution of mercuric chloride, a yellow precipitate is formed of composition $AsH(HgCl)_2$, the reaction being represented by he equation—

$$2HgCl_2 + AsH_3 = 2HCl + AsH.(HgCl)_2.$$

On continuing to pass AsH_3 into the solution the precipitate takes a brown colour, and its composition alters to—

$$AsHg_2Cl + HgCl_2AsH_3 + 3HgCl_2 = 3HCl + AsHg_3Cl_3.$$

The author performs a series of experiments to try to prepare the unknown substance AsH_2HgCl, but without success. However, when AsH_3 is continued to be passed into the alcoholic solution, the brown precipitate is blackened, the substance As_2Hg_3 being formed.—

$$As(HgCl)_3 + AsH_3 = 3HCl + As_2Hg_3.$$

—*Ber. der Deutsch. Chem. Gesellschaft*, 1898, No. 6.

MEETINGS FOR THE WEEK.

Monday, 21st.—Society of Arts, 8, (Cantor Lectures). "Acetylene," by Prof. Vivian B. Lewes.
Wednesday, 23rd.—Society of Arts, 8. "Long Distance Transmission of Electric Power," by Prof. George Forbes, F.R.S.
Friday, 25th.—Physical, 5. "Properties of Liquid Mixtures," by R. A. Lehfeldt. "Certain Diffraction Fringes as applied to Micrometric Observations," by L. N. G. Filon.

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THE CHEMICAL NEWS.
Vol. LXXVIII., No. 2035.

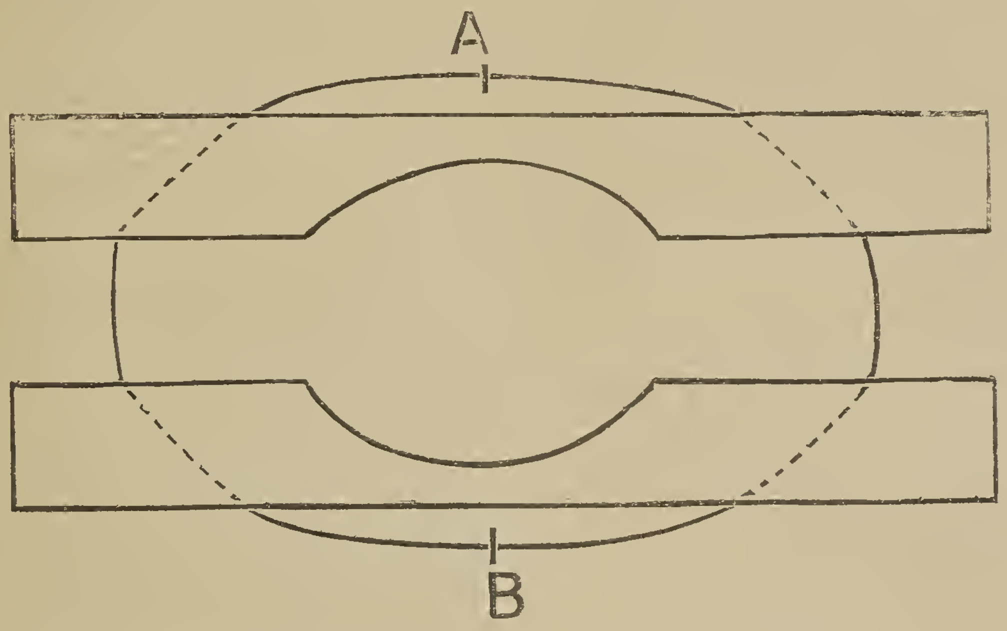
LABORATORY NOTES.

By HORACE JERVIS.

A New Clip.

The accompanying figure is the plan (actual size) of a piece of apparatus which has been devised to suspend flasks in which solutions containing heavy precipitates are being boiled. Such solutions are always in danger of bumping, and when the flasks containing them are solidly supported on the customary tripod they are frequently overturned and sometimes shattered.

The small pieces of wood (⅜″ thick) have a complete circuit of string slackly threaded through oblique holes. The separate ends of another piece of string are attached to A and B, so that, after passing the arrangement over the flask, the suspension by this latter string causes the woods to grip on to the neck, and the flask is just as firmly supported as the neck is strong.



It is obvious that so inexpensive an article may be used in numerous cases where flasks are to be temporarily suspended; all that is needed to complete the equipment being a pencil or pen-holder pushed through the longer string and laid over the hole of a filter-stand.

A rubber ring, to which string is attached, slipped over the neck of a flask, is a very handy way of suspending lighter flasks.

In any case the corrosive action of the steam or vapour from the suspended flask must be taken account of. This difficulty may be partly met for string by soaking it thoroughly in paraffin-wax, tallow, bees'-wax, or oil, rubbing it so as to leave the material in, rather than on, the string. Smooth leather, and particularly porpoise boot-laces, are very durable materials for threading and suspending the arrangement.

Pulp Filters.

Is it too much to reiterate once more the advantage of pulp filters? In some cases, mainly where large sticky precipitates are to be dealt with, the cone filter, plain or ribbed, is very necessary, but for the majority of operations the following characteristics of pulp are highly commendable:—

1. A filtering medium of any desired texture.
2. The greater effect of a given amount of wash water, since every portion thereof passes through the precipitate.
3. No fear that the precipitate will creep over the edges of the paper.

One drawback to the use of pulp is the impossibility of separating the precipitate from the paper. Happily the necessity for such a procedure is comparatively rare, and according to recent publications (Chem. News, lxxviii., 202; and *Zeit. Anal. Chemie*, 1898, xxxvii., 308) it is not necessary in some cases where it has generally been believed to be so.

Having regard to the ignition of a precipitate there is an advantage in the use of pulp in that, by thorough aspiration, the precipitate is sucked firmly on, if not into, the pulp, and is much less likely to spatter if dried rather hurriedly at the muffle's mouth.

In transferring the filter to the crucible—which is done by turning up one edge of the filter with the leg of a forcep, lifting it out, and cleaning with a piece of paper pressed against the revolving funnel—it is frequently impossible to prevent the precipitate touching the crucible at some point. In such ways the glaze of a porcelain crucible is soon destroyed.

To prevent this, it is advisable to place a piece of ashless filter-paper in the crucible and the filter thereon; in this way only the dried precipitate can come into contact with the porcelain, and the brushing out of non-fusible compounds is generally easy and pleasant.

Accelerated Evaporation.

When a solution is being evaporated with a view to ignite the residue, the evaporative surface may be increased by placing a piece of crumpled ashless paper so that it shall be almost wholly above the surface of the liquid. This plan is, of course, not applicable to such solutions as decompose paper.

THE ELECTROLYTIC PREPARATION OF IODOFORM.

By K. ELBS and A. HERZ.

For some years the Chemische Fabrik auf Actien has been manufacturing iodoform, bromoform, and chloroform by the electrolysis of the alkaline or alkaline-earthy chlorides, bromides, and iodides in the presence of alcohol, aldehyd, or acetone. The operation is carried out warm.

For the preparation of iodoform, the electrolyte should be traversed by a current of carbonic acid during the whole of the operation. In fact, the ordinary reaction for the preparation of iodoform is as follows:—

$$CH_3CH_2OH + 10I + H_2O = CHI_3 + CO_2 + 7IH.$$

If this iodine is produced by the electrolysis of an iodide, the alkali set at liberty ought to be saturated; if not, it will again react on the iodoform. It is for this reason that carbonic acid is injected during the operation.

The authors show that the current of carbonic acid can be advantageously replaced by a simple addition of an alkaline carbonate to the electrolyte. In the present note the authors have studied the variations in the return of iodoform according to the temperature, the density of the current, &c., and they come to the following conclusions:—

1. The most favourable temperature is between 60° and 70° C. All other conditions remaining the same, the proportion of hydriodic acid formed increases as the temperature rises.

2. The return of iodoform diminishes if the density of the current exceeds 1 ampère per square decimetre.

3. All other conditions remaining the same, the return of iodoform decreases a little, and the return of hydriodic acid increases a good deal as the proportion of carbonate of soda in the electrolyte is augmented.

4. The best method consists in operating on a solution containing—

Carbonate of potassium	5 grms.
Iodide of potassium	10 ,,
Alcohol	20 c.c.
Water	100 ,,

Every hour the iodoform deposited is collected, and the strength of the solution in iodide of potassium, alcohol, and carbonate of potassium is made up to the standard.

5. The results are much less satisfactory if the alcohol is replaced by acetone. In none of their experiments have the authors obtained pure iodoform. This body was always mixed with iodine and secondary iodised derivatives.

6. Attempts to prepare bromoform and chloroform by the same process have not been successful.—*Zeit. für Electrochemie*, p. 113, 1898.

ON THE DISSOCIATION SPECTRA OF MELTED SALTS.

METALLOIDS: SILICON.

By A. de GRAMONT.

The melted alkaline silicates give, with the usual arrangement of the apparatus already described, a very good spectrum of silicon with a medium condensation of not more than two jars (24 square decimetres). I here give the wave-lengths, corrected to Rowland's scale, I obtained either with the melted salts or with crystallised silicon in a vapour of pure hydrogen.

Si α	636·97	Strong.
	634·22	Very strong.
Si β	597·89	Fairly strong.
	596·03	Easily seen.
Si γ	506·00	Very strong.
	504·55	,,
Si δ	457·57	Very faint.
	456·89	Fairly well seen.
	455·37	Easily seen.
Si ε	413·13 412·92	Fairly strong, very diffuse, and almost united into one band (413·0).

The brightest and most characteristic groups are Si α in the red, Si γ in the green, and Si ε in the violet.

In examining Si γ, it is necessary to be careful not to confound it with a possible apparition of the platinum line 506·04 or with 504·57 of the air. It is for the purpose of eliminating this latter that I examined the silicon spark in hydrogen. The double line Si γ is further, more intense, and has a more diffuse appearance than the corresponding lines of air and of platinum when they appear under the same conditions of experiment.

The group Si δ corresponds to a vague band, 456·5 (Salet), and which M. Lecoq de Boisbaudran observed, as also I did, to be formed of a well-defined triplet.

The fluosilicates also furnish beautiful spectra of silicon. The natural silicates, and in general all non-conducting minerals containing silicon, when reduced to powder and melted with an alkaline carbonate—that of lithium for preference—give, with the condenser spark, not only the silicon lines, but also the spectra of the greater part of the bodies with which they are combined.—*Bull. Soc. Chim.*, Series 3, vol. xix.-xx., No. 13.

ON THE NITRIFICATION OF GLYCERIN WITH NITROUS ACIDS.

By R. AUZENAT.

Since England, by an Order in Council (No. 1, August 5, 1875), decided on the proof to which nitrated explosives intended for import into that country or her colonies should be submitted, this proof, called the heat test, has been adopted throughout the industry.

As is well known, the object of this test is to estimate the time which a certain sensitive paper takes to become discoloured, either by the acidity of the explosive or by the presence of unstable nitric ethers.

In the manufacture of nitroglycerin it is generally admitted that the product obtained with a nitrous nitric acid is so much the richer in unstable sub-derivatives of kinitroglycerin as the proportion of hyponitric acid is greater. Several specialists have also given very different opinions as to the influence exercised by the alkaline washings at a high temperature on the stability of nitroglycerin.

It is in order to throw more light on this question that I undertook the following experiments:—

Nitrifications were made with the same glycerin (of 1·262 density), the same sulphuric acid (at 97 per cent H_2SO_4), and with nitric acids containing the same proportions per cent of HNO_3 (94 per cent) but differing in their proportions of N_2O_4.

The nitroglycerin obtained was washed as usual, first several times with water, then twice with an equal volume of a solution of carbonate of soda at 4 per cent and at 60° C. The nitroglycerin was then washed with distilled water until the alkaline reaction disappeared, and filtered. It is in this state that it was submitted to the heat test; the time noted indicates the precise moment of the appearance of the typical tint on the sensitive paper.

We may as well first mention that the regulations consider as good a nitroglycerin which does not colour the paper before fifteen minutes at 71° C.

No.	N_2O_4 in the nitric acid. Per cent.	Time observed. Minutes.
1.	0·95	2, 2, 2, 2
2.	1·25	55, 55, 55, 55
3.	1·50	55, 63, 63, 72
4.	1·75	46, 46, 48, 48
5.	2·00	42, 42, 43, 47
6.	2·50	38, 38, 42, 42
7.	3·00	30, 30, 30, 34

Although the nitroglycerin No. 1 gave no acid reaction, it was again washed with a solution of 4 per cent of soda at 70° C.; the time observed was then 21, 26, 26, 27 minutes.

The nitroglycerin No. 2 re-washed with soda at 80° C. gave 63, 63, 64, 65 minutes.

No. 3 was washed at 45° C. with water containing 0·5 per cent H_2SO_4; it then had a slightly acid reaction, and answered the test at 54, 56, 56, 57 minutes.

To this same nitroglycerin No. 3, when neutral, I added 0·0006 grm. of nitric acid for each 3·24 grms. of nitroglycerin; the coloration of the paper was immediate. I then added only 0·00006 grm. of nitric acid; the coloration of the paper occurred after nineteen minutes. I increased the quantity of nitric acid again to 0·00012 grm., and the coloration appeared at the end of fourteen minutes.

So from these results we may conclude that:—

a. Although in ordinary practice the proportion of hyponitric acid in the nitric acid is fixed at 2 per cent, we can obtain a nitroglycerin which satisfies the heat test by a nitrification carried out with a nitric acid containing 3 per cent of N_2O_4. However, above 2 per cent decompositions during the nitrification are frequent.

b. The washings with the soda solution at a high temperature increases the stability.

c. Finally, the heat test does not show any sulphuric acid acidity, which is always dangerous if the explosive is to be stored; but it enables us to reject a nitroglycerin containing more than 0·003 per cent of free nitric acid at 71° C., which is a very sensitive indication for such a body. An imperfect washing of the nitroglycerin cannot introduce a sulphuric acidity, since we have used a sulpho-nitric mixture in its manufacture, but the use of an impure absorbent may lead to the presence of a fixed free acid.

It is therefore indispensable to first treat with litmus. If the dynamite has a neutral or alkaline reaction we need not fear the presence of unstable nitric ethers, and in this case the sensitiveness of the test is sufficient.—*Moniteur Scientifique*, Series 4, vol. xii. (second part), Sept., 1898.

PRACTICAL CHEMISTRY.

By GEORGE GEORGE, A.I.C., F.C.S.

I. *A New Flask.*

In the preparation of organic compounds it is often necessary to pass into a liquid, which is kept boiling in a flask connected with a reflux condenser, a gas, which either has some direct chemical action upon the liquid or is simply used to drive out air, and thus prevent oxidation. For example, in the preparation of benzalchloride, chlorine is passed into boiling toluene.

In such an experiment the flask used has to be provided with an exceptionally large neck, in order that the inner tube of the condenser and the tube which is conducting in the gas may both pass through the cork. The flask A (Fig. 1) has been found to be much more convenient. The neck is of an ordinary size, whilst the tube B is fused into the side of the neck These flasks can be obtained from any glass-blower at a cost practically the same as that of the ordinary distilling bulb of the same size.

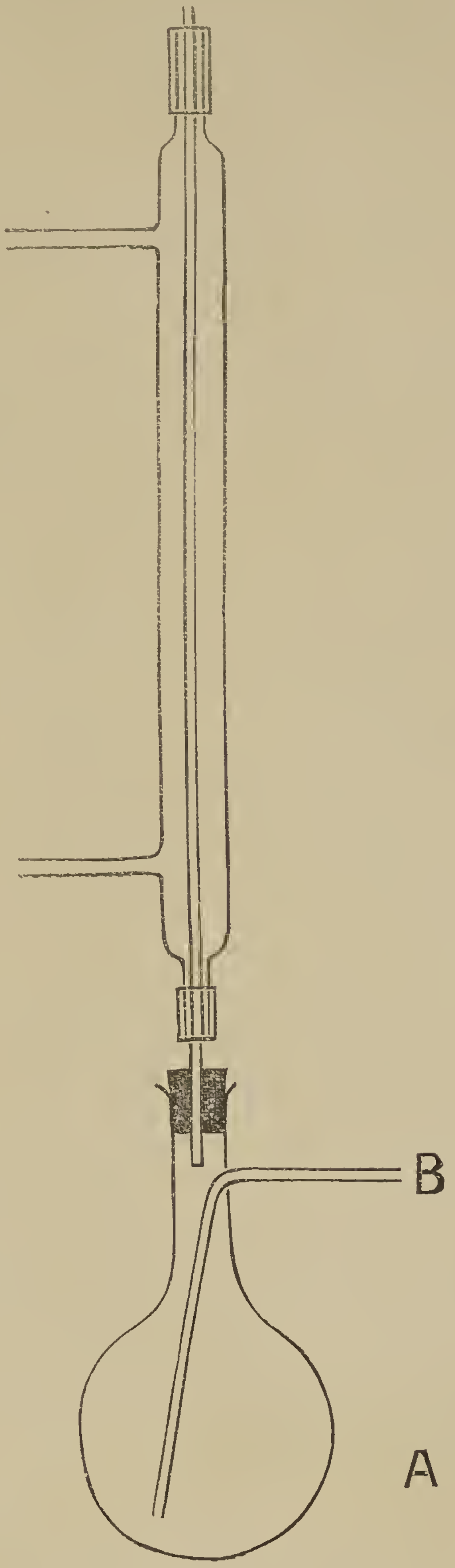


Fig. 1.

II. *Composition of Magnesium Oxide.*

In determining the composition of magnesium oxide, by heating magnesium in a porcelain crucible, unless great care is taken the results are not good, owing to the loss of oxide, and also to the formation of a quantity of nitride. A much better piece of apparatus to use than a crucible is a glass tube, as shown in Fig 2. The tube, which is about 10 c.m. long, is made from hard glass tubing of 1 c.m. diameter. The end D is drawn out, and this end is packed with dry asbestos wool (A). At C, a cork containing a small tube is fitted, whilst the magnesium is placed about the middle of the tube (B). Air or oxygen is aspirated through the tube, whilst the portion at B is heated by means of the Bunsen. The asbestos arrests any oxide that is carried over by the current of air. The experiment may be varied by using copper foil or precipitated copper.

Allan Glen's School
(Glasgow and W. of Scotland Technical College).

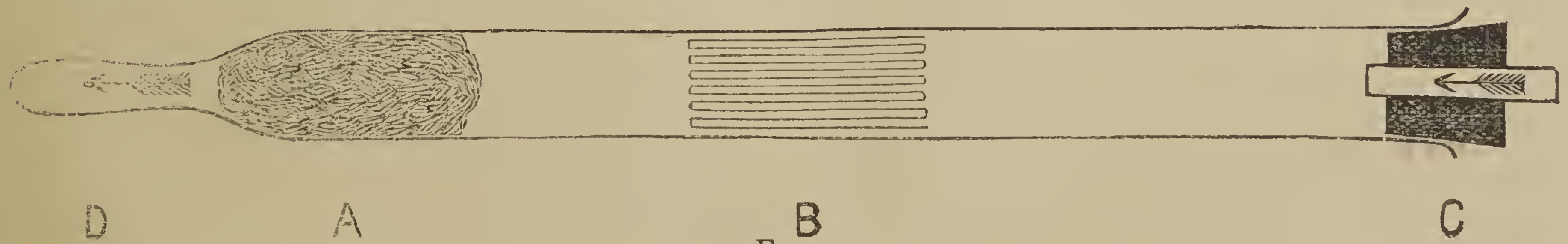


Fig. 2.

Note on Drown's Method of Determining Silicon in Steel.—George Auchy.—The author modifies Drown's method by conducting the evaporation with aqua regia and sulphuric acid, instead of sulphuric and nitric acids. He claims a great gain in accuracy as well as practical convenience.—*Journ. American Chem. Soc.*, vol. xx., pp. 547—549.

THE EXTRACTION OF NICKEL FROM ITS ORES BY THE MOND PROCESS.*

By Professor ROBERTS-AUSTEN, C.B., D.C.L., F.R S., Assoc. Inst. C.E.

THE Mond process marked an entirely new departure in metallurgical practice and in the principles which had hitherto guided it. It depended on the remarkable property possessed by nickel of forming a volatile compound with carbon monoxide, from which metallic nickel might be released if the gaseous compound was heated to 180° C.

The methods hitherto employed for extracting the metal from its ores involved concentrating the nickel either as a sulphide (matte or regulus), or as arsenide (speise), followed by either dry or wet treatment; and the metal had to be refined, mainly with a view to separate it from associated carbon.

In 1889, Dr. Ludwig Mond, in collaboration with Dr. Carl Langer, had been engaged upon a method for eliminating the carbon monoxide from gases containing hydrogen. They had been guided by the observation that finely-divided nickel removed carbon from carbon monoxide at a temperature of 350° C., converting it into carbon dioxide, whereas the dissociation of carbon monoxide by heat alone, according to Victor Meyer and Carl Langer, remained incomplete at the high temperature of 1690° C. The experiments were carried out in conjunction with Dr. Friedrich Quincke; finely-divided nickel, formed by reducing nickel oxide at 350° C. by hydrogen, being treated with pure carbon monoxide in a glass tube at varying temperatures. The gas escaping from the apparatus was ignited, and while the tube containing the nickel was cooling, the flame became luminous, and increased in luminosity as the temperature sank below 100° C. Metallic spots were deposited on a cold plate of porcelain held in this luminous flame, and on heating the tube through which the gas was escaping a metallic mirror was obtained, while the luminosity of the flame disappeared. These metallic deposits were found to be pure nickel. Nickel carbonyl was then isolated in a liquid state, and it was possible to produce it with facility in any desired quantity. It could be readily distilled without decomposition, but on being heated to 150° C., the vapour was completely dissociated, pure carbon monoxide being obtained and the nickel being deposited in a dense metallic film upon the sides of the vessel.

No other metals which were submitted to investigation showed indications of combining directly with carbon monoxide except iron. The discovery that in a mixture of metals only nickel and iron would form volatile compounds with carbon monoxide, and that they could, therefore, be separated from the other metals, induced Dr. Mond to arrange experiments with ores containing nickel, cobalt, iron, and copper—such as "kupfernickel" and "pyrrhotine." The experiments afforded such promising results that apparatus of considerable size, though still within the limits of the resources of a laboratory, was set up, and in it several pounds of ore could be treated with carbon monoxide. The principal nickel ores which were metallurgically treated contained the nickel in combination with arsenic and sulphur, besides other metals and gangue. These ores had first to be submitted to calcination, in order that the nickel might be present in the form of oxide, and to drive off, as far as practicable, the arsenic, sulphur, and other volatile bodies. The resulting oxide of nickel was treated with reducing gases, such as water-gas or producer gas, in order to convert the oxide of nickel into finely-divided metallic nickel, and the material containing it was cooled to about 50° C., and was treated with carbon monoxide.

In 1892 an experimental plant on a large scale had been erected at Smethwick, near Birmingham. The process began with "Bessemerised" matte; it ended with the market product, commercial nickel. The Bessemerised matte proceeded to the first operation of dead roasting, after which the matte contained 35 per cent of nickel, 42 per cent of copper, and about 2 per cent of iron. It then passed to the second operation for the extraction of part of the copper (about two-fifths) by sulphuric acid, the copper being sold as crystallised sulphate of copper. The residue from this process contained about 51 per cent of nickel, and it passed to the third operation for reducing the nickel. Incidentally, the remaining copper was reduced to the metallic state, care being taken to avoid reducing the iron. This was effected in a tower provided with shelves, over which mechanical rabbles passed, the reducing agent being the hydrogen contained in water-gas. The temperature did not exceed 300° C., and should be kept lower when much iron was present. From this tower the ore was conveyed continuously to the fourth operation of volatilisation, in which part of the nickel was taken off by carbon monoxide and formed the compound nickel-carbonyl. The formation of this volatile compound was effected in a tower similar to the reducing tower, but the temperature was much lower, and did not exceed 100° C. From the volatiliser, the ore was returned to the reducer, and it continued to circulate between the reducing and the volatilising stages for a period which varied between seven days and fifteen days, until about 60 per cent of the amount of nickel had been removed as nickel-carbonyl. The residue from this operation, amounting to about one-third of the original calcined matte, and not differing much from it in composition, was returned to the first operation and naturally followed the same course as before. The nickel-carbonyl produced in the fourth operation passed to a decomposer, which consisted either of a tower or a horizontal retort heated to a temperature of 180° C., so as to decompose the nickel-carbonyl and release the nickel in the metallic form, either on thin sheets of iron, or, preferably, on granules of ordinary commercial nickel. Carbon monoxide was in turn also released, and was returned to the volatiliser for taking up a fresh charge of nickel. When the operation was in progress, the gaseous carbon monoxide and the partially reduced oxide of nickel and copper continuously revolved in two separate circuits, which joined and crossed each other in the volatiliser. The commercial product contained 99·8 per cent of nickel.

The author proceeded to a description of the working as he saw it in full operation in Smethwick a few months ago. The plant had been working for some time, and about 80 tons of nickel had already been extracted from different kinds of matte. The results were quite satisfactory, and pointed to the conclusion that the process was well able to compete with any other process in use for the production of metallic nickel.

The process would always occupy a prominent position in chemical history, and there appeared to be no reason why it should not play an important part in metallurgical practice. Its application in Canada to the great nickeliferous district of Sudbury would probably contribute to the development of the resources of the great Dominion.

Azimidic Combinations of Benzimidazols.—St. von Niemetowski.—In a previous communication, the author showed that, by the action of nitric acid on the orthoamidobenzimidazols, new compounds were formed, which he called azimides of the benzimidazols. He now describes many of their properties, and notes that the facility with which the avimidic chain is broken differentiates these compounds from the true azimides, which are characterised by great stability. They have further studied the azimides of (β) orthoamidophenylbenzimidazol, of (β) orthoamidophenyl, &c., as well as the action of bromine on these azimides, and the nitric colouring matters derived from them.—*Berichte der Deutschen Chemischen Gesellschaft*, xxxi., 1898.

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* Abstract of a Paper read before the Institution of Civil Engineers, November 8, 1898.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 3rd, 1898.

Professor Dewar, F.R.S., President, in the Chair.

Messrs. L. M. Nash, A. J. Parker, W. A. Lethbridge, F. E. Weston, and W. C. Reynolds were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Hugh Poynter Bell, 30, Egerton Crescent, S.W.; Reginald Arthur Berry, The University Chemical Laboratory, Cambridge; Thomas Henry Boardman, 4, St. George's Terrace, Wilton, Taunton; Marston Taylor Bogert, 259, Broadway, Flushing, New York; Arthur Brooke, 17, Cavendish Square, Hull; Johannes Christian Brunnich, Agricultural College, Gatton, Queensland; John Paul de Castro, Ford House, Redruth, Cornwall; David Leonard Chapman, Hulme Hall, Plymouth Grove, Manchester; William Samuel Crouch, Colombo, Ceylon; Alfred Valentine Cunnington, Christ's College, Cambridge; William Brown Davidson, 29, Bedford Street, Liverpool: Samuel Dickson, The Kraal, Elm Road, New Maldon; Francis Alfred Drake, Rivington and Blackrod Grammar School, Horwich, Lancs.; James Edward Ferguson, 26, Connaught Road, Stroud Green, N.; John Naish Goldsmith, Rock House, Tunbridge Wells; E. B. Hadley, The Green, Calne, Wilts; John Haworth, 4, Horsdon Terrace, Tiverton, Devon; Alexander Garden Hendry, 14, Avenell Road, London, N.; George William Fraser Holroyd, 14, Kensington Garden Terrace, W.; Walter Howe, 45, Spring Gardens, Bradford; Thomas Hill-Jones, Eagle Wharf Road, London; Reginald Arundale Kay, 7, The Causeway, Cambridge; John Charles Mascarenhas, 35, Harold Road, Upton Park; Thomas Arthur Nightscales, Tynemouth Street, Hull; William Pollard, Hitchin, Herts; John Armstedt Ray, jun., 15, Nassau Street, Dublin; Edmund Milton Rich, 7, Therapia Road, Honor Oak, S.E.; Gilbert Rigg, Tudor Villa, Bryn Road, Swansea; Henry John Rolfe, 8, Powis Square, Bayswater, W.; Richard Seligman, 15, Queen's Gate Gardens, S.W.; George Senior, Arwendon, Abergele, North Wales; Samuel Smiles, jun., Fairoak, Beckenham, Kent; Benjamin Jordan-Smith, 42, King's Road, Reading; Basil Steuart, Broxburn, near Edinburgh; Ambrose Walton, Gledholt, Lower Broughton Road, Broughton; John Henry Young, 115, Birmingham Road, Oldbury.

The President said that before passing to the ordinary business of the meeting, he desired, on behalf of those present, to express condolence with the family of the late Mr. J. A. R. Newlands in their bereavement. It was not the occasion to refer to the work of Mr. Newlands in detail; everyone would recognise, however, that his name would always be associated with the progress of chemical thought in our time, and, happily, he had lived to witness the expansion of the idea contained in his law of octaves into one of the most comprehensive developments of modern chemical theory. As a tribute to his memory, it was proposed that an enlarged portrait of Mr. Newlands should be hung in the Society's rooms.

Of the following papers those marked * were read:—

*117. "*Determination of the Equivalent of Cyanogen.*" By George Dean, B.A.

An examination of the different values found for the atomic weight of nitrogen led to the attempt to deduce it in another way, viz., from the equivalent of cyanogen. A known quantity of dry silver cyanide, prepared by precipitation of dilute silver sulphate solution with dilute hydrocyanic acid, was dissolved in nitric acid, and the silver determined by finding what amount of pure potassium bromide was necessary for its complete precipitation. Stas's method of titration in a beam of yellow light was employed. The weight of cyanide corresponding to the atomic weight of silver was thus found; subtracting from this the atomic weight of silver, the equivalent weight of cyanogen was obtained. The result of the experiments performed was to give a value of 26·065. Thus cyanogen is added to those substances—*e.g.*, chlorine, bromine, iodine, &c.—whose equivalents have been observed by direct comparison with silver. If the value 12·01 is assumed to be the atomic weight of carbon, that for nitrogen, calculated from the equivalent of cyanogen, is 14·055.

Discussion.

The President referred to the great importance of determining atomic weights by indirect methods. In conjunction with Dr. Scott, he had estimated the molecular weight of triethylamine hydrobromide by titrating purified triethylamine with hydrobromic acid (*Proc. R. S.*, 1883, xxxv., 347). The values obtained showed differences which were easily recognisable, the best determination giving 182·012, and the mean 182·089 for the molecular weight. This proved that triethylamine could not as yet be obtained sufficiently pure for the purpose of a determination comparable in accuracy with Stas's determination of the ammonium salt; but in spite of the relatively wide limits, it was possible to deduce the atomic weight of carbon from these values by a method entirely independent of the combustion of carbon as diamond, graphite, or carbonic oxide, on which all previous determinations of the atomic weight of carbon had been based. Thus subtracting Stas's value for the molecular weight of ammonium bromide (98·032), the values for C_6H_{12} became 83·98 and 84·057 respectively, which lead to 11·981 and 11·993 as the atomic weight of carbon if Stas's value for hydrogen (1·008) be employed. Stas, curiously enough, had never deduced the atomic weight of hydrogen from his values for ammonium and nitrogen. The probable explanation of this was that he believed the deduced result, O:H=16:1·008, to be far too high, being unable to reconcile it with the determination O:H=16;1, which Dumas obtained from the synthesis of water. If, however, the atomic weight of hydrogen be taken as unity, Stas's values for oxygen and nitrogen become 15·86 and 13·92 respectively, and it was to be remembered that, according to Lord Rayleigh, the densities of hydrogen and nitrogen were in the ratio of 1 to 13·898. Mr. Dean's experiments gave for the atomic weight of nitrogen a value slightly higher than this, and almost identical with that deduced by Stas for his synthesis of fused nitrate of silver. He hoped Mr. Dean would continue this important research.

*118. "*The Composition of American Petroleum.*" By Sydney Young, D.Sc., F.R.S.

An investigation has been made of the hydrocarbons in American petroleum boiling between, say, 25° and 115°, and evidence has been obtained of the presence of the following:—

Isopentane, b. p. 27·95°; normal pentane, b. p. 36·3°; pentamethylene, b. p. about 50°; isohexane, b. p. about 61°; normal hexane, b. p. 68·95°; methylpentamethylene, b. p. about 72°; benzene, b. p. 80·2°; hexamethylene, b. p. 80·8°; isoheptane, b. p. 90·3°; normal heptane, b. p. 98·4°; methylhexamethylene, b. p. about 102°; toluene, b. p. 110·8°. Of these, the two pentanes and normal hexane have been obtained pure, normal heptane nearly so, and hexamethylene and isoheptane fairly pure. Miss E. C. Fortey, B.Sc., has obtained hexamethylene nearly pure from American and quite pure from Galician petroleum (*Proc.*, 1898, xiv., 103). It is not improbable that other isomeric hexanes, and, therefore, possibly heptanes, may be present, and there are indications of the existence of small quantities of dimethylpentamethylene in American petroleum. A comparison of the results obtained with American, Galician, and Russian petroleum shows that the same classes of hydrocarbons—paraffins, polymethylenes or naphthenes, and aromatic hydrocarbons—are present in the petroleum from all three sources, but that the relative amount of naphthenes, and, in all probability, of aromatic hydrocarbons, is greatest in Russian and least in American petroleums.

*119. "*The Separation of Normal and Iso-heptane from American Petroleum.*" By Francis E. Francis, B.Sc., Ph.D., and Sydney Young, D.Sc., F.R.S.

The heptanes cannot be separated in a pure state from petroleum by fractional distillation, owing to the presence of naphthenes with boiling-points not sufficiently far removed from those of the two paraffins.

A large quantity of mixed heptanes containing naphthenes, obtained by the partial fractionation of American petroleum, was therefore brominated. Heptyl and isoheptyl bromides were separated by fractional distillation under reduced pressure with a twelve-column dephlegmator, and were reduced in alcoholic solution by a copper-zinc couple, a small amount of saturated hydrochloric acid being added. The reduced hydrocarbons were purified as far as possible, but the quantities — especially that of isoheptane—were too small to admit of satisfactory fractionation.

The boiling-points and specific gravities of both paraffins were determined, also the critical constants of normal heptane, and its vapour pressures and specific volumes at a few temperatures. The data are compared with those for Thorpe's specimens of normal and isoheptane.

*120. "*The Boiling-points and Specific Gravities of Mixtures of Benzene and Normal Hexane.*" By D. Hamilton Jackson, M.A., Ph.D., and Sydney Young, D.Sc., F.R.S.

In the fractionation of American petroleum from which the aromatic hydrocarbons have not been removed previously by treatment with a mixture of sulphuric and nitric acids, it is noticed that the benzene comes over chiefly at about 65°, the fractions above and below this temperature containing smaller and smaller amounts of it.

The approximate estimate of the amount of benzene is easily obtained by treating the fractions repeatedly with mixed nitric and sulphuric acids and diluting the acid with water. The dinitrobenzene separates after some time in needle-shaped crystals. The most probable explanation of the lowering of the boiling-point of benzene appeared to be that aromatic hydrocarbons and paraffins, though miscible in all proportions, approximate in their behaviour to partially miscible liquids. The results obtained show that this is the case, for there is always expansion on mixing, and the boiling-point of normal hexane is hardly raised by the addition of even 10 per cent of benzene, whilst that of benzene is very rapidly lowered by adding hexane.

It is therefore impossible to separate pure normal hexane by distillation of any mixture of this paraffin with benzene, though it is easy to separate pure benzene from a mixture containing only a moderate amount of hexane.

*121. "*The Action of Fuming Nitric Acid on the Paraffins and other Hydrocarbons.*" By Francis E. Francis, B.Sc., Ph.D., and Sydney Young, D.Sc., F.R.S.

In the separation of pure normal hexane from American petroleum, the methyl pentamethylene was removed by heating the nearly pure hydrocarbon with fuming nitric acid during several days. It was observed at the same time that the low boiling fractions, containing isohexane, were also purified by this treatment, and that, on diluting the nitric acid, considerable quantities of a trinitro-derivative of isohexane separated as a crystalline solid.

Other isoparaffins were found to react rapidly with fuming nitric acid when heated on a water-bath, and to yield liquid or solid nitro-compounds, but the normal paraffins were attacked only very slowly, and in these cases the acid, when diluted, did not become turbid. Details are given of the action of fuming nitric acid on isopentane, isohexane, isoheptane, iso-octane, and diisobutyl.

The behaviour of the paraffins, when heated with fuming nitric acid, is compared with that of other classes of hydrocarbons.

Discussion.

Mr. Groves asked to what extent olefines were present in petroleum.

Mr. Davis referred to Worstall's statement that normal hexane yields a considerable amount of the primary nitro-derivative when boiled with fuming nitric acid during a long period (*Amer. Chem. J.*, 1898, xx., 202), and asked whether this had been observed by the authors, as such a method of purifying normal hexane would appear to be rather destructive.

Professor Young, in reply, said that the olefines present in American petroleum must be inconsiderable in amount, as very little bromine is required to produce a permanent colouration; they would, of course, be eliminated during the treatment with mixed nitric and sulphuric acids.

With respect to the action of nitric acid, it must be remembered that the result is greatly influenced by the conditions; thus Konowaloff had shown that normal hexane and normal octane yield secondary nitro-compounds on heating with dilute nitric acid under pressure. Dr. Francis and he had found that the isoparaffins undergo nitration readily when heated with fuming nitric acid in a reflux apparatus on a water-bath. The normal paraffins were much more slowly attacked under similar conditions, and as the nitric acid remained clear on dilution, it was evident that nitro-compounds had not been formed from them in any appreciable quantity.

*122. "*A Composite Sodium Chlorate Crystal in which the Twin Law is not followed.*" By William Jackson Pope.

The author describes a composite crystal of sodium chlorate deposited from a pure aqueous solution. It consists of a cube-shaped crystal growing on to a tabular one; both crystals show the form $\{100\}$; a three-fold axis of symmetry of the one coincides in direction with a four-fold axis of symmetry of the other, and the plane (011) on the former is parallel to the plane (010) on the latter. The composite crystal is thus not developed in accordance with the ordinary twin law, and yet the two crystalline individuals have grown together in a highly symmetrical manner.

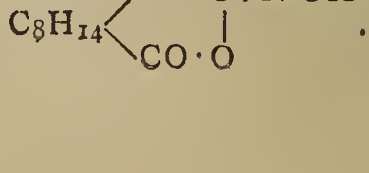
*123. "*Stereoisomeric Bromonitro- and Chloronitrocamphors.* By T. Martin Lowry, B.Sc.

The action of nitric acid on bromocamphor and on chlorocamphor leads to the production of only one nitrobromo- and nitrochloro-camphor. The action of bromine and of chlorine on an alkaline solution of nitrocamphor yields in each case, however, a mixture of stereoisomerides, similar to that which is produced by the action of bromine on chlorocamphor (*Trans.*, 1898, lxxiii., 569). The stereoisomeric bromonitro- and chloronitro-camphors, isolated from this mixture, have the following melting-points and specific rotatory powers:—

	M. p.	$[\alpha]_D$(chloroform).
α-Chloro-α′-nitrocamphor	95°	− 5°
α′-Chloro-α-nitrocamphor	132	+13
α-Bromo α′-nitrocamphor	107	−22
α′-Bromo-α-nitrocamphor	106	+53

*124. "*Camphoryloxime* (*Camphonitrophenol*). By T. Martin Lowry, B.Sc.

The so-called "camphonitrophenol," produced by boiling nitrocamphor with concentrated hydrochloric acid, is shown to be an oxime of camphoric anhydride, identical with that obtained by the interaction of hydroxylamine with camphoric anhydride. Its constitution is probably that represented by the formula—



$$C_8H_{14}\left\langle\begin{array}{l}\text{—C : N·OH}\\ \quad\;\;\;|\\ \text{CO·O}\end{array}\right. .$$

125. "*The Formation of Ethereal Salts of Polycarboxylic Acids.* By S. Ruhemann and A. V. Cunnington.

The authors have found that the condensation of ethylic malonate and its homologues with the ethylic salts of unsaturated acids, leading to the formation of those of polycarboxylic acids, is readily brought about by adding a small quantity of sodium ethoxide (0·5 grm.) to the mixture of ethereal salts. In a number of cases the combination is accompanied by an evolution of heat, the intensity of which appears to depend on the negative character of the salts entering into reaction.

The preparation of a number of salts of polycarboxylic acids by this method is described, and the conclusion is drawn that in the same measure as the negative character is diminished by the introduction of an alkyl radicle into ethylic malonate or the ethylic salt of the unsaturated acid, so does the heat evolved in the reaction decrease.

126. "*Note on the Action of Light on Platinum, Gold, and Silver Chlorides.*" By E. Sonstadt.

The action of direct sunlight on very dilute solutions of potassium chloroplatinate is similar to that of prolonged heating, platinum monochloride being separated, as described in an earlier paper (*Proc.*, 1898, xiv., 25). The action of bright sunshine is, however, slower and feebler than that of heat. Solutions of gold chloride, if sufficiently dilute, are more readily affected by light than corresponding platinum solutions. An aqueous solution containing about 0·04 per cent of gold chloride required exposure to bright sunshine for a day or two before any action was perceptible, and the reduction was incomplete even after exposure during several weeks. A more dilute solution, containing 0·007 per cent of gold chloride, became distinctly bluish after a few hours' exposure, and the blue colouration deepened day by day until a deposit formed, which was blue by transmitted light, and afterwards assumed the usual brown colour of precipitated gold, the liquid being left colourless. A trace of hydrogen peroxide was detected in the liquid. The reaction may therefore be considered to be the same in this case as when a very dilute solution of auric chloride is decomposed by heat (Chem. News, 1898, lxxvii., 74).

It seemed probable that the action of light on silver chloride would, like the decomposition of platinum and gold chlorides in dilute solution by the action of heat or of light, depend on the presence of water and the formation of hydrochloric acid and hydrogen peroxide. Some silver chloride, precipitated from solution of silver nitrate by hydrochloric acid, was thoroughly washed by agitation with repeated portions of water, and decantation, the operations being conducted by feeble gas light, and then exposed under water to direct sunlight, with frequent agitation. After some days the supernatant water was examined, and was found to contain a very appreciable quantity of hydrochloric acid, and to give a faint reaction for hydrogen peroxide. One of the two formulæ which will satisfy these conditions is—

$$6AgCl+4H_2O=2Ag_2Cl+2Ag+2H_2O_2+4HCl.$$

But as silver, set free molecularly in presence of hydrochloric acid, would, on a reasonable presumption, form silver chloride with liberation of hydrogen, and as the nascent hydrogen would react on part of the hydrogen peroxide to form water, the equation, with these corrections, becomes—

$$6AgCl+4H_2O=2Ag_2Cl+2AgCl+2HCl+2H_2O+H_2O_2.$$

The same series of reactions would occur with the reformed silver chloride and water; and it is obvious that, as, at each stage of the reaction, one-third of the silver chloride and one-half of the water are reproduced, and similarly with the hydrochloric acid and hydrogen peroxide, it follows that when the silver chloride taking part in the reaction is completely converted into argentous chloride, water will still be left as a permanent residue in addition to hydrochloric acid and hydrogen peroxide. This assumes that the silver chloride in a condition of accessibility to the influence of light is in the exact proportion to the water present indicated in the equation. But if the attackable silver chloride is present in a certain excess over that required by the equation, the end products of the series of reactions may be represented by the simple equation—

$$4AgCl+2H_2O=2Ag_2Cl+2HCl+H_2O_2,$$

in which no residue of water appears. This is the second of the two possible formulæ referred to, and, it may be asked, what need is there to assume the complex reactions in series following from the first formula, when the second, which is so much simpler, satisfies the experimental results? There are, however, other experimental results of a singular character to be described, which may possibly be considered to be more easily intelligible on the supposition that the reactions are of the serial nature involved in the first equation.

Some silver chloride, precipitated and washed as already described, was dried for several hours on a sand-bath, the temperature being raised progressively until the chloride became adhesive. Although the process was conducted under very feeble gas light, the chloride was sensibly discoloured. This discolouration is probably due to the same reaction taking place between moisture and the chloride under the influence of a high temperature as is effected by light in the cold. It appears that a higher temperature is needed for the reaction than that of water boiling at ordinary pressure, as the chloride is not discoloured by heating under water. A thoroughly dry and heated glass tube was nearly filled with the hot chloride, and immediately sealed. Another portion of the chloride was put into a bulb tube which had been previously dried and strongly heated, and was fused in the bulb. A slight, but unmistakable, trace of moisture condensed on the sides of the tube, showing that the chloride was not perfectly dry. The tube containing the (imperfectly) dried silver chloride was exposed to direct sunshine, when a bluish tint instantly spread over the chloride, deepening to a rusty brown, but leaving patches unaffected, so that, after long exposure, the fragments presented a mottled appearance with white spots on a dark ground. Evidently, portions of the chloride were really dry, though the bulk was not so, the dry portions resisting the action of light. Another tube, rather long and narrow, was similarly filled with the dried chloride, sealed, and exposed to sunshine with about half its length covered. The exposed portion of the chloride darkened as in the former case, with patches remaining unaffected. The covering was then shifted over the previously exposed part of the tube, with a like result; but the darkened chloride, now sheltered from light, became slowly bleached, until it was quite white. On again reversing the conditions, the bleached portion darkened and the coloured portion was bleached, the same happening on each subsequent reversal. Even in the portion of the tube exposed to bright sunshine, the chloride on the under side became partially bleached, and on turning the tube round, the effect, after a few hours, was reversed. Dry silver chloride was then placed in the central part of a phial tube, and was protected by a little recently ignited asbestos from contact with fragments (placed in its lower and upper parts) of calcium chloride, and of caustic soda taken from sodium that had been long kept in a loosely closed bottle. The well-closed phial was kept in the dark during two or three days, to give time for absorption of moisture, and was then exposed to sunshine. The silver chloride became coloured, with white spots remaining unattacked, as in the former cases: but, on transference to a dark place, or on shading a portion, there was no bleaching. The colouration remained practically constant in light and in shade. The bleaching effect, or the re-formation of argentic from argentous chloride under the conditions described in the former case, must therefore be attributed to a reversal in the dark of the primary reaction which takes place in the light,—a reversal made impossible in the last-mentioned case by the absorptive action of the calcium chloride and the soda. Hydrochloric acid has no bleaching effect on light-altered silver chloride suspended in water, either in darkness or in light.

127. "*Methane Trisulphonic Acid.*" By Ernest H. Bagnall, B.Sc.

In endeavouring to prepare the various sulphonic acids and sulphones of dichlorobenzidine by the action of fuming sulphuric acid on dichlorodiacetylbenzidine, a substance was obtained which proved to be identical with methanetrisulphonic acid (Theilkuhl, *Annalen*, 1868, cxlvii., 134). This acid is also formed by a like process from diacetylbenzidine, acet-α-naphthalide, and acetanilide, the last giving a remarkably good yield of the substance. The silver salt crystallised in small, white, iridescent, monhydrated, orthorhombic plates, $a:b:c = 2\cdot9152:1:0\cdot5422$. The copper, barium, calcium, potassium, sodium, and ammonium salts are also described.

Attempts were made to prepare the corresponding sulphonic acids of ethane and propane by a similar process, but without satisfactory results.

128. "*The Nutrition of Yeast.*" By Arthur L. Stern, D.Sc.

This investigation was undertaken to determine the amount of inorganic and nitrogenous nutriment required to produce the largest crop of yeast, the greatest assimilation of nitrogen, and the most complete fermentation in a fixed time. During the course of the investigation other points had to be considered, of which the most important was the part played by sulphur compounds on yeast nutrition. The earlier work of Hayduck, who employed a different variety of yeast and a different variety of sugar, is referred (*Zeitschrift fur Spiritusind.*, 1881, 173).

The yeast employed was a pure form obtained from a Burton pitching yeast, the sugar was *d*-glucose, the nitrogenous nutriment asparagine, and the inorganic nutriment of two kinds,—the first prepared from a yeast ash and free from sulphur, the second a mixture of potassium phosphate, magnesium sulphate, and calcium sulphate. Each experiment consisted in fermenting 500 c.c. of a 10 per cent solution of the sugar, to which varying amounts of the nitrogenous and inorganic nutriment had been added.

It is shown that sulphur is an essential constituent of yeast nutriment, and that in the absence of other more suitable forms of sulphur nutriment, sulphates can supply the yeast with this element, a portion of the sulphate being invariably reduced to sulphuretted hydrogen. Attempts were made to find a substance of known constitution which could supply yeast with sulphur without the evolution of sulphuretted hydrogen, but without success.

It has been asserted that iron is an essential constituent of yeast nutriment, but no evidence could be obtained in support of this statement.

The author has examined the effect of variation in the amount of (1) nitrogen nutriment and (2) inorganic nutriment respectively on the amount of nitrogen assimilated, the percentage of nitrogen nutriment assimilated, the percentage of nitrogen contained in the yeast, the percentage of sugar remaining unfermented, and the weight of the yeast crop, and draws the following conclusions;—Any increase of nutriment beyond a definite limit will not materially increase the amount of nitrogen assimilated by the yeast, the percentage of nitrogen in the yeast, the weight of the yeast, or the amount of sugar fermented. This limit, called the normal supply, is the largest quantity that the yeast can assimilate under the conditions employed in the experiments, and is approximately 0·025 grm. of inorganic nutriment per 100 c.c., and the same weight of nitrogen supplied as asparagine.

(To be continued).

NOTICES OF BOOKS.

Lighting by Acetylene. Generators, Burners, and Electric Furnaces. By William C. Gibbs, M.E. London: Crosby Lockwood and Son. New York: D. Van Nostrand Company. 1898. Pp. 141.

The production of carbide of calcium on the large scale, and by its means the subsequent production of acetylene gas, is a comparatively recent industry—and, in fact, lighting by acetylene is as yet only in its infancy. The question of generators to safely keep up a constant supply of acetylene without any intermission has not yet been solved in a perfectly satisfactory manner; but many experimenters are at work, and new schemes, as well as improvements on old ones, are constantly being brought out.

Acetylene was discovered by Edmond Davy in the year 1836; but it is only within the last few years that the commercial production of calcium carbide has brought acetylene within the range of practical utility.

The dangers attending the use of acetylene have no doubt been unduly exaggerated; heat, flame, the electric spark, or even the electric arc itself, will not produce an explosion at the ordinary atmospheric pressure; nothing but the detonation of fulminate of mercury or other violent explosive will bring this about. But when the gas is compressed, it becomes more and more unstable as the pressure increases, until the point of liquefaction is reached, when it becomes exceedingly dangerous. The use of copper must be absolutely prohibited in any apparatus or fittings with which the gas may come in contact—acetylide of copper being very explosive.

Many methods for preparing and utilising acetylene gas are fully described in this volume, the text being interspersed with numerous illustrations.

A considerable amount of space is devoted to generators, which are divided into three classes:—1st. Those which have a separate gas holder, and in which the water is supplied gradually and in measured quantity to a considerable portion of carbide; 2nd, those which contain both the carbide and the water, with means for successively immersing and withdrawing the carbide; and 3rd, those in which measured quantities of the carbide can be dropped into a large quantity of water.

Towards the end of the book, the requirements of the New York Board of Fire Underwriters are given in full, both with regard to the installation and use of acetylene gas generators, and for the storage of a limited supply of calcium carbide. There is also an imposing list of patents taken out in the United States in connection with the subject; it fills six pages in small type.

There is, we are sorry to see, no index, and the chapters are not numbered. The book is, however, well got up, and contains a great deal of valuable information.

Health Notes, and Curiosities of Medical Science. By Dr. T. L. Phipson. London: George Routledge and Sons, Lim. 1898. Pp. 205.

The volume now before us gives, in an interesting and popular manner, a large amount of information with regard to health and the way to keep healthy, &c.

The book is divided into thirty-five chapters, and includes a great variety of subjects, such as the value of trees in towns from the hygienic point of view; the tobacco question with regard to disinfection—in this chapter we read that smoking is forbidden in German bacteriological laboratories, as tobacco acts injuriously on bacterial cultivations. The intelligence of beasts is an interesting chapter, as is also the one on skin grafting.

Chapter X. gives a full account of the invention and development of the thermometer, which was used in medicine two hundred and forty years ago.

The subject of "hypnotism" and "suggestion" is discussed in Chapter XIV. Cases are mentioned of surgical operations having been successfully performed without the use of chloroform, the patient being first put into a mesmeric sleep. A most remarkable case of "suggestion" is cited, where a youth is told to warm his arm at a *cold* stove; he, thinking that the stove is hot, puts his arm too near it, and actually burns himself badly, a severe blister being formed surrounded by a zone of inflammation, *just as if it had been placed in close proximity to a hot stove.* We think this tale must be taken with a certain amount of salt.

Insanity and sunstroke are treated in Chapters XVII. and XVIII., and in Chapter XXII. we come to the great water question. We are glad to see that the author has no reason to complain of the water supplied by the London water companies; it is probably the best supply in the world, and certainly no other supply is so carefully and constantly controlled and kept up to the highest standard of purity by daily chemical and bacteriological examinations.

A curious and valuable statement is to be found in Chapter XXXI. to the effect that in Normandy, where cider is practically the sole and universal beverage, the medical practitioners have *never met with a single case of stone, gravel, or calculus* during an experience of over forty years.

The book is well printed on good paper, and will well repay reading.

CORRESPONDENCE.

THE GASES OF THE ATMOSPHERE.

To the Editor of the Chemical News.

Sir,—In a Lecture delivered on the 8th of this month, at the meeting of the Pharmaceutical Society, Professor Ramsay is reported to have made the following statement:—

"Early in 1894 Lord Rayleigh wrote to *Nature*, announcing what appeared to him to be an anomaly, namely, that whilst atmospheric nitrogen was a little over fourteen times as heavy as hydrogen, nitrogen prepared from ammonia or from other chemical compounds was slightly lighter, the difference being about 1 in 230. No explanation was forthcoming at the time, but Lord Rayleigh talked the matter over with several of his friends, including the lecturer, who had some time before suggested to him, at his request, a method of preparing nitrogen by passing a mixture of air and ammonia over red-hot copper, when the oxygen united with the hydrogen of the ammonia, and the nitrogen from both the air and the ammonia passed on. He suggested to Lord Rayleigh that probably atmospheric nitrogen was not as pure as it was supposed to be, and directed his attention to Cavendish's experiments and the residue he had found when combining nitrogen with oxygen. Lord Rayleigh did not at first attach much weight to the suggestion, and thought it more likely that different compounds contained different kinds of nitrogen."

I have on previous occasions noted in your columns the progressive eclipse of Lord Rayleigh by the other member of the binary star of Argon, but I confess I was rather surprised to find him thus finally reduced to the position of the dark attendant.

On turning to Lord Rayleigh's account of the same period, given on April 5, 1895, at the Royal Institution, some rather remarkable discrepancies are revealed. Lord Rayleigh stated that, "about this time last year or a little earlier," he had been led, by his own purely physical experiments, to ask himself what was the evidence that all the so-called nitrogen of the air was of one quality? He put that question not to Professor Ramsay, but to his colleague Professor Dewar. "His answer was that he doubted whether anything material had been done upon the matter since the time of Cavendish, and that I had better refer to Cavendish's original paper." Lord Rayleigh added that he quickly followed Professor Dewar's advice, and found to his surprise that Cavendish had put the question quite as sharply as he could put it himself, and had moreover endeavoured to answer it by an appeal to experiment. He then went on to make it absolutely clear that Professor Ramsay did not appear upon the scene at all until after Lord Rayleigh, acting upon Professor Dewar's information, had found in the experiment of Cavendish the solution of his problem, and had recognised in the Cavendish residue the unknown substance hitherto confounded with nitrogen, whose presence explains the greater density of "nitrogen" obtained from the atmosphere. Hence the evidence of Lord Rayleigh given more than three years ago directly controverts the story Professor Ramsay now tells.

Again, Professor Ramsay says that "early in 1894 Lord Rayleigh wrote to *Nature*" stating the discrepancy he had found between the weights of atmospheric and chemical nitrogen, and asking chemists for suggestions. I thought it well to verify this reference. Lord Rayleigh wrote no such letter to *Nature* early in 1894. It was on Sept. 29, 1892, that the letter in question appeared. The correction is important because in his lecture, and still more distinctly in his book on the gases of the atmosphere, Professor Ramsay conveys the impression that this letter immediately led to his "asking and obtaining permission" to study atmospheric nitrogen. He tells us in the book that he began this study by passing nitrogen from the air over red-hot magnesium, and that the first weighing of a portion of gas so treated took place in May, 1894. It is obvious that this story loses considerably in plausibility when we know that the letter appeared eighteen months previously.

Did Professor Ramsay before May, 1894, ask and obtain Lord Rayleigh's consent to his concurrent investigation of atmospheric nitrogen? There is no evidence whatever for the statement. The real sequence of events I suggest is as follows:—The letter in *Nature* in 1892 had nothing to do with the matter except as an *ex post facto* excuse. In April, 1894, Lord Rayleigh read at the Royal Society a paper "On an Anomaly encountered in Determination of the Density of Nitrogen Gas." At the same time tne Smithsonian Institution was offering a prize for the most important discovery in connection with the atmosphere. Professor Ramsay took Lord Rayleigh's proof that there is some inert gas in the air which is not nitrogen, and proceeded in his own way, and without saying a word about it, to isolate and study this body. At the same time—that is, between April and July, 1894—Lord Rayleigh was pursuing the line of the Cavendish experiment, isolated the unknown gas, examined its spectrum, and showed it privately to some of his friends. It was when he was thus maturing a discovery practically made some time before, that Professor Ramsay, probably about the middle of July, came down upon him with another set of researches, springing, like his own, from the results published by himself on April 19. It can easily be understood that, as stated in Professor Ramsay's book, letters passed between them almost daily. The net result was that at the meeting of the British Association, in August, the discovery was announced in their joint names. It will be conceded, I think, that Lord Rayleigh paid heavily for the suggestion made to him two years earlier by Professor Ramsay, that he could obtain nitrogen by passing a mixture of air and ammonia over red-hot copper. From the way it is put in the lecture one might fancy that Professor Ramsay invented that bit of text-book knowledge for the occasion.

In his book on the gases of the atmosphere, Professor Ramsay, by dint of a narrative chronologically confused and a judicious abstention from precise dates, managed to convey a general impression that he had done important and even decisive work before Lord Rayleigh had got as far as the Cavendish experiment. But he has now gone a step further, and has tried to make it appear that everything was due to his direct inspiration. If the myth goes on evolving itself at the present rate, Lord Rayleigh will shortly figure as a sort of humble assistant called in by Professor Ramsay to perform the routine work of burning away the nitrogen.

Lord Rayleigh has apparently elected to say as little as possible about the manner in which Professor Ramsay became his collaborator, but he has never admitted the accuracy of Professor Ramsay's version. One thing, however, he is quite explicit about—that the inert ingredient of the atmosphere, isolated by Cavendish, was re-discovered by himself, and recognised as something not nitrogen, before Professor Ramsay had anything to do with the matter.—I am, &c.,

Suum Cuique.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvi., No. 3, July 18, 1898.

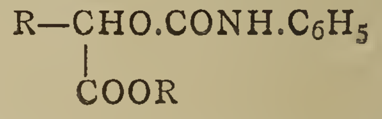
Researches on the Relations existing between Luminous Energy and Chemical Energy.—M. Berthelot.—A measure of the light energy transformed into chemical energy is best obtained by investigation of endothermic reactions, including the phenomena of oxidation or of combination, where heat is evolved. The author examines the following endothermic reactions:—Decomposition of (1) nitric acid; (2) pure iodic acid; (3) hydriodic acid; (4) oxide of mercury. Also he makes experiments on the reduction of silver chloride. All these observations take place at ordinary temperatures in—(1) direct solar light; (2) diffused light; (3) darkness. The numbers are given in the various cases.

Anhydrous and Crystallised Sulphide of Magnesium.—A. Mourlot.—The author prepares amorphous sulphide of magnesium by the action of carbon disulphide on magnesium at a red heat. The crystalline form is obtained from this by fusing it in the electric furnace, or it can also be made by the action of tin sulphide on anhydrous magnesium chlorine. In properties it differs from the amorphous form in being much more stable. It resembles crystalline barium sulphide in most of its reactions. It can, however, be easily distinguished, as it cannot be reduced by carbon.

Decomposition of Barium and Calcium Phosphate by Water at 100°.—Georges Viard.—Varying weights of the phosphate are placed in the same volume of water and kept for five hours in a vessel of boiling water. The liquid is then filtered from the crystalline precipitate which is formed. Both filtrate and precipitate are analysed. It is found that the decomposition becomes more and more slow as the concentration increases. In fact the substance behaves in precisely the same way as when placed in cold water, which action was investigated by Joly; the difference being in the numbers for the ratio of the total phosphoric acid to the combined acid, the limits being 2 at 15° and 2·8 at 100°.

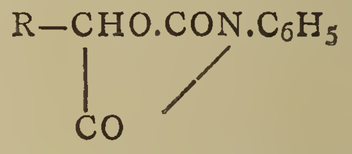
The Substituent Action of the Halogens upon each other in the Aromatic Series.—V. Thomas.—In a recent publication the author has shown that the whole series of substitution products of benzene, up to the compound C_6Cl_6, can be obtained by chlorination of benzene with ferric chloride, and that similar derivatives of benzene homologues, such as toluene, and of bodies with more complex molecules, *e.g.*, naphthalene, are also obtainable. Brominated benzenes also give rise to a series of chlorinated substitution products when acted upon by ferric chloride, *e.g.*, the compound C_6H_4ClBr. parabromochlorobenzene, the chlorination of which is here discussed. The ferric chloride exchanges its chlorine for the bromine of the organic bromide; an unusual phenomenon in the aromatic series, but one which is well known in the fatty series, when the chlorinating agents are metallic chlorides, such as $SbCl_5$, PCl_5, $HgCl_2$, &c. The reaction under discussion is between paradibromobenzene and ferric chloride; more than one product is obtained, each being derived from chlorination of $C_6H_4ClBr(1.4)$, but that produced in the greatest quantity corresponds to the formula C_6BrCl_5. Thus there are two stages in the reaction, viz., substitution of one bromine atom and chlorination. It is not yet determined in which order these operations occur.

Diketones of the Tetra-hydro-β-oxazol Derivatives of the Phenylurethanes of certain Oxy-acids.—E. Lambling.—The author has demonstrated the production of urethanes of the general formula—

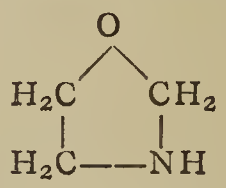


$$\begin{array}{l} R\text{—}CHO.CONH.C_6H_5 \\ \quad\quad | \\ \quad\;\; COOR \end{array}$$

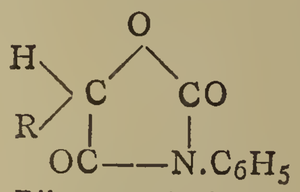
by the action of phenyl isocyanate upon esters of hydroxy-acids. The free acids are obtained by saponification with soda and subsequent decomposition of the sodium salt with acid. On boiling these acids with water, internal anhydrides are produced of the type—



which represent diketones of tetra-hydro-β-oxazol—



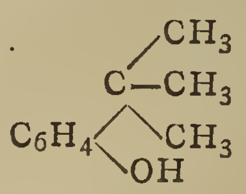
Tetra-hydro-β-oxazol.



Diketones obtained.

The author has obtained such diketones from phenylurethanes of lactic, trichlorlactic, glycolic, phenylglycolic, and α-oxyisobutyric acids. Descriptions of the properties of these substances are given.

Action of Bromine in presence of Aluminium Bromide on Para-isobutyl-phenol. Remarks on the Bromination of Phenols.—F. Bodroux.—The author has already studied the action of an excess of bromine in presence of aluminium bromide on certain phenols. He now concludes by applying the reaction to a compound possessing a long side chain, viz., para-isobutyl-phenol—



A description of the method is given and of the properties of the resulting compound. The melting-point together with the result of an estimation of the bromine it contains show that the principal product is pentabromophenol. Hence the molecule of the isobutylphenol has been split up by the action of excess of bromine in presence of aluminium bromide. The conclusion drawn is that the same rules apply, on bromination, to both hydrocarbons and phenols as regards (1) substitution of the hydrogen atoms of the benzene nucleus, and (2) replacement of the side chain—if the latter is attached by $(C)^{iv}$ or $(CH)'''$—by a bromine atom. If, on the contrary, the side chain is attached by a $(CH_2)''$ group it is not destroyed. Thus, in the case of certain phenols, bromination may serve to determine the constitution of the side chain.

Vol. cxxvii., No. 4, July 25, 1898.

Determination of Arsenic in Antimony and other Metals.—O. Ducru.—Already inserted in full.

Composition of Phosphorescent Sulphides of Strontium.—José Rodriguez Mourelo.—In a former paper, the author stated that monosulphide of strontium is a non-phosphorescent substance. The object of his present research is to determine what impurities cause it to appear phosphorescent. The sulphide is prepared in two ways:—1. By the reduction of celestine containing calcium sulphate and sodium chloride, in addition to strontium sulphate, by pure carbon. The resulting sulphide phosphoresces with a dull green colour. 2. By similarly treating an artificial strontium sulphate, made by precipitating nitrate of strontium with a solution of sodium sulphate. This sulphide, when pure, gives no phosphorescence, but the phosphorescence begins when sodium sulphide, sodium chloride, and strontium sulphate are added; the proportion of the latter being increased until phosphorescence ceases.

Estimation of Methyl Alcohol in Ethyl Alcohol.—A. Gautier.—The author describes a colorimetric method of detecting and estimating methyl alcohol in ethyl alcohol by means of oxidation. The reactions of the pure alcohols were first studied separately, when oxidised with potassium bichromate and sulphuric acid. Besides acetic aldehyd and acetic acid, the distillation products contained, in the one case ethylal, $CH_3.CH{<}\genfrac{}{}{0pt}{}{C_2H_5O}{C_2H_5O}$, and in the other, methylal, $CH_2{<}\genfrac{}{}{0pt}{}{CH_3O}{CH_3O}$. In order to distinguish between these two ethers, they were condensed with dimethylaniline. The resulting compounds were—(1) $C{<}\genfrac{}{}{0pt}{}{H}{CH_3}=\left(C_6H_4N{<}\genfrac{}{}{0pt}{}{CH_3}{CH_3}\right)_2$, which on oxidation gave a blue coloration, rapidly disappearing under the influence of heat; and (2) $CH_2=\left(C_6H_4N{<}\genfrac{}{}{0pt}{}{CH_3}{CH_3}\right)_2$, viz., tetramethyldiamidodiphenylmethane, which on oxidation gave an intense blue coloration, deepening under the influence of heat. By this method, a quantity of methyl alcohol not exceeding 0·5 per cent can be detected in absolute alcohol. A source of error is due to the presence of methyl alcohol existing as an impurity in the dimethylaniline, and an account is given of the means by which this is avoided.

Berichte der Deutschen Chemischen Gesellschaft.

Vol. xxxi., February 28, 1898.

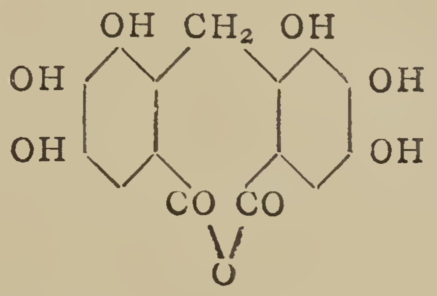
On Fluorescent Bodies.—Br. Pawlewski.—It has been laid down that, besides the anthracene derivatives and those containing sulphur and nitrogen, all fluorescent bodies should also contain a pyronic nucleus surrounded by complex atoms, and a phthalic residue. The author shows that though this theory applies to the combinations of the group of fluorescein, it is not quite the same for many other bodies. He gives as examples resorcinbenzene, allofluorescein, and benzylgaïacol. He has recently prepared a substance which possesses a very strong fluorescence; 1 part in 31,250,000 through a thickness of 15 c.c. showing a distinct fluorescence.

Products of Condensation of Furfurol and Furfuracrolein.—H. Röhmer.—The author has prepared several products of condensation, among which may be mentioned *furalpyruvic acid*, $C_4H_3O.CH=CH.CO.COOH$, obtained by the condensation of furfurol with pyruvic acid in the presence of glacial acetic acid; *furalphenylacetic acid*, $C_4H_3O.CH=C{<}\genfrac{}{}{0pt}{}{C_6H_5}{COOH}$ in silky needles; the *piperide* of this acid $C_4H_3O.CH=C{<}\genfrac{}{}{0pt}{}{C_6H_5}{CON.C_5H_{10}}$. He has also prepared *furfuracrolein-acetophenone*,—

$$C_4H_3O.CH=CH.CH=CH.CO.C_6H_5,$$

which crystallises in dilute alcohol in needles fusible at 52—53°; *furfuracrolein-acetic acid*, in needles of a faint yellow colour melting at 153—154°; and finally, *semicarbazide of furfuracrolein*, prepared by dissolving 2 grms. of furfuracrolein in water and adding 2 grms. of hydrochlorate of semicarbazide and 2 grms. of acetate of potassium; it crystallises in alcohol and melts at 215—219°.

Products of the Reaction of Formic Aldehyd on Gallic Acid.—R. Möhlau and L. Kahl.—By this reaction the authors have succeeded in isolating a substance by heating a mixture of 2 molecules of gallic acid and 1 molecule of formic aldehyd with fifteen times the quantity of dilute hydrochloric acid (1 : 5). The substance is a crystallised methylene-digallic acid, difficultly soluble, of which the anhydride, $C_{15}H_{10}O_9$, has been analysed, and probably corresponds to the following constitutional formula—

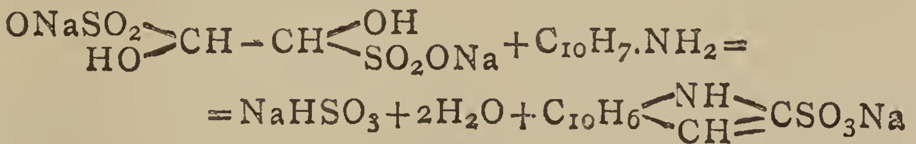


This acid dissolves in concentrated sulphuric acid with a yellow colour, turning a cherry red by the action of nitric acid; its alkaline solution takes a red colour when exposed to the air.

On Formaldehyde-trioxyfluorone-dicarbonic Acid.—R. Möhlau and L. Kahl.—If we dissolve methylene-digallic acid in concentrated sulphuric acid and heat slowly, the yellow solution takes a green colour at about 50°, then an intense blue; the acid in question, $C_{15}H_{15}O$, appears in the form of a crystalline violet powder, and constitutes a colouring matter for mordants. The acetyl-derivative melts at 140·5—141·5°, at the same time turning brown; its benzoyl-derivative crystallises in alcohol in colourless prisms melting at 250·5—252·5°. The tetracetyl derivative is in the form of brilliant flakes melting at 241°.

The Final Product of the Action of Chloride of Nitrogen on Dimethylaniline.—W. Hentschel.—The author has previously obtained a compound, $C_{24}H_{13}Cl_{19}N_2$, by this method. He now finds that he can obtain the same body more easily by saturating a 30 per cent solution of dimethylaniline in benzene, first with hydrochloric acid, then with chlorine, and finally with an excess of chloride of nitrogen, keeping the whole for some hours away from the light. The crystalline mass thus formed is freed from the ammonium compounds by washing with water, and the aqueous solution is shaken up with benzene, which, on being left, gives a crystalline salt on evaporation. The purified product melts at 117°.

Synthesis of the Naphthindol Derivatives.—O. Hinsberg and A. Simcoff.—The easy formation of indolsulphonic acids according to the equation—



$$\genfrac{}{}{0pt}{}{ONaSO_2}{HO}{>}CH-CH{<}\genfrac{}{}{0pt}{}{OH}{SO_2ONa}+C_{10}H_7.NH_2=$$
$$=NaHSO_3+2H_2O+C_{10}H_6{<}\genfrac{}{}{0pt}{}{NH}{CH}{\geqq}CSO_3Na$$

induced the authors to experiment on β-naphthindolsulphonic acid, and in the endeavour to transform it into the principal derivatives of the series β-naphthindol. They here describe the methods adopted by means of which they have prepared several of these bodies.

MISCELLANEOUS.

Messrs. John J. Griffin & Sons.—Notice of Removal.—This old-established firm have recently removed from their premises at 22, Garrick Street, Covent Garden, into buildings which have been specially constructed for their work, at 20-26, Sardinia Street, Lincoln's Inn Fields. This has been rendered necessary owing to increasing work, which has demanded larger and more adapted buildings, the workshops in Sardinia Street being considerably extended.

Royal Institution.—The Christmas Course of Lectures, specially adapted to young people, at the Royal Institution, will be delivered this year by Sir Robert Stawell Ball, LL.D., F.R.S., Lowndean Professor of Astronomy and Geometry in the University of Cambridge. The subject will be "Astronomy," and the lectures (which will be illustrated by models and the optical lantern) will deal with the sun, the moon, the inner planets, the great planets, shooting stars, and new methods. The first lecture will be delivered on Tuesday, December 27th, at 3 o'clock, and the remaining lectures on December 29th and 31st, 1898, and on Ianuary 3rd, 5th, and 7th, 1899.

The Edinburgh University Chemical Society met on November 14th, when Prof. Crum Brown delivered the Presidential Address. Prof, Crum Brown gave a short sketch of Kolbe's life, and reviewed his work under the following heads:—Sulphone Acids; Joint Work with Frankland on the Nitriles; Relation of the Alcohols, Aldehyds, Acids, and Ketones to one another; Electrolysis of Organic Salts; Oxyacids. He specially pointed out the remarkable originality and independence of Kolbe's work and speculation, and their bearing on modern theories of chemical constitution.

International Exhibition of Electricity.—An International Exhibition of Electricity and the Silk Industry will be held at Como in 1899, to celebrate the centenary of Volta's great discovery, Como being his native city. In this Exhibition the history of a century in the vast field of electricity will be reviewed, and a congress of electricians will discourse on the most recent progress of the science. The silk industry is a trade much developed in Como, and it is considered that it would be interesting to show the application of electric energy to an important series of machine tools. Scientific men and engineers from all parts of the world will, it is hoped, take part in the Congress. The Exhibition will be divided into twelve sections, besides the Honours class.

Electrolysis of Bromides and Alkaline Fluorides.—H. Pauli.—The author has repeated, on the bromides and alkaline fluorides, Œttel's experiments on the chlorides. The law for the formation of hypobromides and bromates appears to be sensibly the same as that which regulates the formation of the hypochlorites and chlorates. On the other hand, the electrolysis of the alkaline fluorides has not given any oxygenated salts. The solution after electrolysis contains peroxide of hydrogen, formed according to the equation—

$$Fl_2 + 2KHO = 2KFl + H_2O_2.$$

The presence of peroxide of hydrogen was recognised by the ether and chromic acid reaction.—*Zeit. für Electrochemie*, 1898, No. III., p. 474.

MEETINGS FOR THE WEEK.

Monday, 28th.—Society of Arts, 8, (Cantor Lectures). "Acetylene," by Prof. Vivian B. Lewes.

Wednesday, 30th.—Society of Arts, 8. "Photographic Developers and Development," by C. H. Bothamley, F.R.S.

Thursday, Dec. 1st.—Chemical, 8. "Oxidation of Polyhydric Alcohols in presence of Iron," by H. J. H. Fenton, M.A., and H. Jackson, B.A., B.Sc. Ballot for the Election of Fellows.

THE CHEMICAL NEWS.

VOL. LXXVIII., No. 2036.

RUTHENIUM TETROXIDE: AN EXPLOSION.

By JAS. LEWIS HOWE.

It may be worth while to call attention to an explosion which occurred recently in this laboratory in connection with work on ruthenium tetroxide. As is well known, the only satisfactory method of obtaining pure ruthenium is that of passing a rapid current of chlorine through a solution of the melt obtained by fusing crude ruthenium with caustic potash and saltpetre. The distillate, which consists of RuO_4, is generally received in dilute alcoholic potash, the ruthenium being precipitated as a hydroxide. In the case noted the distillate was collected in a small flask for the purpose of obtaining the RuO_4, the excess of chlorine and RuO_4 being led into dilute alcoholic potash, the amount of alcohol being about 10 per cent. After some 5 grms. of RuO_4 had been collected the chlorine tube became stopped up, and the alcoholic potash solution sucked back into the flask containing the RuO_4. In a moment there was a very violent explosion, the apparatus being completely shattered. The force of the explosion can be judged by the fact that a splinter of the thin flask was driven through a thick glass bottle standing near by, making a hole about 3×1 m.m., but not breaking and hardly cracking the bottle. One is reminded of the accident in Deville's laboratory, when nearly 100 grms. of RuO_4 in process of distillation exploded with terrific violence. RuO_4 is so rapidly reduced by organic substances that, if any considerable quantity is present, the heat of the reaction causes instantaneous decomposition. A drop of RuO_4 coming in contact with rubber, wood, or many other organic substances, instantly explodes. On the other hand, in the distillation with chlorine, the RuO_4 can be received apparently with perfect safety in dilute alcoholic potash.

The dense black smoke produced when RuO_4 explodes is readily soluble in hydrochloric acid, and hence probably consists of Ru_2O_3. When RuO_4 in a liquid condition is brought in contact with a lump of sulphur, the latter becomes gradually covered with a black deposit, and in the course of a few moments an explosion takes place. Here the sulphur seems capable of reducing RuO_4, a fact hitherto unnoticed.

Chemical Laboratory of the Washington and Lee
University, Lexington, Virginia.

NOVEL PRODUCTION OF VORTEX MOTION.

By C. S. STANFORD WEBSTER, F.I.C., F.C.S.

When the freshly gathered leaves of the native Eucalyptus tree (*Eucalyptus globulus*) are ignited. they project vortex rings in considerable numbers in succession, accompanied by a spluttering noise. The best results are obtained by holding the scythe-shaped leaf vertically and igniting the apex,—this being the part where the greatest number of translations are obtained. The leaves experimented upon were some very fine specimens of San Remo production.

Possibly in the production of these vortex rings, blisters are first formed by the extrusion of the cuticular tissues, and, on the blisters bursting, air or aqueous vapour is spontaneously liberated, the rings being rendered visible on their contact with the smoke from the burning external portion of the leaf. The leaves of the small English variety of *Eucalyptus* possess similar properties to the native product, but in a lesser degree, the rings projected being insignificant in size, comparatively speaking.

It is of course quite immaterial in the production of vortex rings whether the smoke or vapour be inside or outside the apparatus, as can easily be demonstrated by placing an empty Tait's apparatus (this consists of a box with a large round hole at one end, the other extremity being covered with a tense sheet of caoutchouc) suddenly in front of a dense cloud of ammonium chloride vapour, and striking the caoutchouc sheet at the same moment,—a vortex ring is formed, being rendered visible after its translation through the vapour.

The author uses the vapour obtained by heating the solid ammonium chloride, in preference to the usual method in which the two constituents are placed side by side, since the vapour thus obtained is not only denser, and more agreeable to work with, but can be kept under complete control.

If desired to fill the Tait's apparatus with the vapour, the solid is heated in a wide glass tube, one end of which is connected directly with the box by means of caoutchouc tubing, and to the other end a narrow glass tube is attached, and bent back parallel with the volatilising tube, so that the same flame heats both simultaneously; this narrow tube then terminates in a long caoutchouc tube used for blowing into. By gently blowing into the glass apparatus the respired air is heated, and at the same time drives the volatilising ammonium chloride into the box, which is quickly filled with the vapour.

POTASSIUM FERRO- AND FERRICYANIDES AS REAGENTS.

By ROBERT MELDRUM, F.C.S.

Molybdenum.

$K_3Fe(CN)_6$, no result with acid or alkaline solutions, even on boiling.

$K_4Fe(CN)_6$, with acid solutions deep brown colour, discharged to a colourless solution by NH_4HO. This test is reliable to the extent of 1 in 50,000, and is very characteristic. AsH_2S gives with 1 in 50,000 a decided brown colouration; $Zn+HCl$, no result; $Zn+HCl+KCNS$, a red colouration; it will be seen that the reagent is a delicate one. With neutral solutions, on boiling a dirty green precipitate results, which on adding NH_4HO drop by drop is turned blue, and is latterly dissolved to a yellowish green opalescent solution on the addition of more alkali. Reliable to the extent of 1 in 400, though a precipitate results on boiling with a much weaker solution than this. Either reagent is preferable to sodium hydrogen phosphate.

Cadmium.

$K_4Fe(CN)_6$, white precipitate; unchanged on boiling, soluble in NH_4HO, insoluble in dilute acids.

$K_3Fe(CN)_6$, yellow precipitate; unchanged by boiling, soluble in NH_4HO or HCl, insoluble in H_2SO_4 or acetic acid. The ferricyanide is the more delicate and distinct of the two tests, the precipitate of which, in solutions containing less than than 1 in 2000, appears white. This I find to be a useful reagent for cadmium salts, and consider it superior to H_2S.

Silver.

$K_3Fe(CN)_6$, brick-red precipitate, changing to dirty yellow colour on boiling, soluble in NH_4HO, but insoluble in HNO_3.

$K_4Fe(CN)_6$, white precipitate, unchanged by NH_4HO; turned green by boiling, which is turned brown by NH_4HO. The precipitates are not soluble in excess of reagent. Reliable only for strengths up to 1 in 400.

Gold.

$K_4Fe(CN)_6$, no result in cold; but on boiling yields green colouration, discharged by NH_4HO and forming a yellow precipitate, partly soluble in excess to a yellow solution.

$K_3Fe(CN)_6$, no result till on adding few drops of NH_4HO, when dirty yellow precipitate forms, insoluble in excess. Not reliable for solutions weaker than 1 in 300, and, therefore, is not so useful as the ordinary tests.

Platinum.

$K_3Fe(CN)_6$, no result with acid or alkaline solutions, even on boiling.

$K_4Fe(CN_6)$, with 1 per cent solution gives heavy crystalline precipitate, forming a dark green liquid on boiling; turned black by NH_4HO. A few drops of the reagent added to a 0·2 per cent solution and boiled produces very dark green solution, appearing almost black. On boiling with excess of reagent a light green precipitate results, which NH_4HO turns olive-green, then yellow, and as more $K_4Fe(CN)_6$ is added forms a yellow solution. The green precipitate is soluble in HCl, forming a very strong indigo-blue liquid: by this means less than 1 in 5000 may be detected. The other tests are good for 1 in 1000. These reactions have been found of some use in qualitative work.

Mercury.

Mercuric Salts.—$K_3Fe(CN)_6$ gives no result in cold solutions, but on boiling a dark green solution is formed, which on dilution and addition of NH_4HO throws down dirty yellow precipitate.

$K_4Fe(CN)_6$, a white precipitate, soluble in excess; on adding more reagent it becomes a pale yellow, and on heating turns to a brilliant green, which NH_4HO changes to a flesh-colour. These tests hold good for solutions of 0·25 per cent strength. None of them are so delicate and useful as KI.

Mercurous Salts.—$K_3Fe(CN)_6$, light brown precipitate; turned green by boiling, and on adding NH_4HO yellow.

$K_4Fe(CN)_6$, white precipitate; changing to grey on boiling, and black by NH_4HO. These reactions are distinct with 0·25 per cent solutions.

Lead.

$K_3Fe(CN)_6$, no precipitate; on adding NH_4HO yields dirty yellow precipitate, which on boiling becomes pale yellow.

$K_4Fe(CN)_6$, white precipitate; not changed by boiling or NH_4HO, insoluble in acetic acid. Both reliable for 0·2 per cent solutions of lead acetate.

Zinc.

$K_4Fe(CN)_6$, white precipitate; insoluble in HCl, or NH_4Cl, or NH_4HO.

$K_3Fe(CN)_6$, yellow "ochre" precipitate; soluble in NH_4HO, also in hot HCl. This is a most useful and satisfactory reagent for zinc, as the usual reagents, NH_4HO, $(NH_4)_2S$, NaHO, Na_2CO_3, and KCN, all yield white precipitate, and hence Al, which gives no precipitate with $K_3Fe(CN)_6$ or $K_4Fe(CN)_6$, is much easier distinguished from Zn by this means.

The Examination of Blood Stains.—We are requested to state that at the meeting of the Society of Public Analysts to be held on Wednesday Evening next, December 7th, an illustrated lecture will be delivered by Mr. A. H. Allen, F.I.C., of Sheffield, on "The Use of the Micro-Spectroscope, and the Methods of Detecting Blood in Chemical-Legal Investigations." Any persons who may be interested in the subject are invited by the Council to attend. Intending visitors who will not be introduced by members of the Society are requested to apply for tickets to Mr. E. J. Bevan, Hon. Secretary, 4, New Court, Lincoln's Inn, London, W.C.

LABORATORY NOTES.

By WM. FRENCH, M.A., F.I.C.

Equivalents of Metals.

In comparing the equivalents of some metals with that of oxygen (by conversion to oxide) for class work, I have adopted the following method, which I find is easily performed and possesses none of the difficulties of loss by "spurting," &c., with the advantage that, as a rule, the whole class can obtain fairly concordant results.

About 1 grm. of metal (copper, tin, &c.) is placed in a hard glass test-tube (6″×¾″) which is loosely closed with recently ignited asbestos fibre, and weighed. The plug is carefully removed, sufficient nitric acid is added to dissolve the metal, and the plug replaced. The tube is now placed on a sand-bath, sloping at about an angle of 30°, and heated to remove excess of acid. When dry, the tube is strongly heated over a naked flame, taking care to heat the whole of the tube in turn. Cool, re-weigh, and calculate in the usual way. A glass-wool plug will also do.

Working with a class of twelve students, as a mean of ten results the number 31·91 was obtained for the equivalent of copper, the whole of them being very near to that number. For tin the results have been equally concordant, but not quite so near to the number obtained by a more accurate method.

Possibly this method is in use, but it certainly is not common, and I would recommend those who have not tried it as a class experiment to do so in preference to the usual crucible or inverted funnel method so generally figuring in the text-books.

Bury Grammar School.

ON THE DISSOCIATION SPECTRA OF MELTED SALTS.

METALLOIDS: CARBON.

By A. de GRAMONT.

As with the metalloids already described, it is difficult to obtain the carbon lines in melted salts. But if the melted carbonated salt is taken out of the flame, the carbon lines appear, as do also the air lines, and their brightness appears to increase with the length of the spark—that is to say, with the increase of the difference of potential. Being desirous, however, of keeping the spark on the melted salt very short, so as to do away with—or diminish—the air spectrum, I intercalated in the secondary circuit of the coil an exciter with an adjustable attachment, to enable me to establish a sufficient difference of potential in the discharge from the condenser (which was formed of a variable number of Leyden jars).

By keeping the melted salt in a pasty state of fusion, a little above the flame, we can see the appearance of the spectrum of the carbon lines in a very distinct manner. I have compared it with that of free carbon, either in Siberian graphite and in retort carbon; this latter, however, even after treatment with acids, continued to give numerous other lines, due to impurities (Ca, Ba, Fe, &c.).

The Siberian graphite from the Alibert mines, on the contrary, gave only the carbon spectrum, the spectrum of the lines and bands of Swan mixed together, as well in perfectly dry air and carbonic acid as in pure hydrogen. But I have never found a trace of the Swan bands in the melted salts, where the carbon lines only were associated with those of the metal. It appeared to me important to make observations of a band spectrum, associated with a line spectrum, under electrical conditions, where, up to the present, spectra of dissociation only remained.

Below are given the carbon lines I obtained with the carbonates, placed in accord with the observations of previous experimenters with free carbon (see Table).

So as to be quite certain as to the origin of the lines,

	Free Carbon.				Melted Carbonates.		
	Angström and Thalén.	*i.*	Eder and Valenta.	*i.*	A. de Gramont.	*i.*	
C α. ..	658·40	10	658·42	1	—		Not seen.
	657·85	12	657·87	1	657·85	7	Very distinct.
	569·51	6	Not photographed.		—		Not seen.
Group I.	566·19	6			566·22	3	Easily seen.
	564·75	8			564·86	3	,,
	563·96	2			564·10	2·5	,,
	538·0	2	539·98	2	537·99	5	Fairly well seen.
Group II.	515·14	5	516·12	1	515·16	7	Very distinct.
	514·50	6	514·49	1	514·46	7	,,
	513·38	3	513·37	1	513·29	7	,,
	Not seen.		455·63	1	—		Not seen.
C β ..	426·66	10	426·75	4	426·70	9	Strong, wide, very diffuse.

I made observations in pure hydrogen with the condenser spark on carbonates of lithium and potassium melted on a platnium spiral made incandescent by means of an electric current, thus operating in an atmosphere entirely free from all carbonated gases. I felt, however, sure that in the previous experiments the spark above the Bunsen burner did not give any carbon lines beyond those in the carbonate.

The values given in the accompanying table have been corrected to the normal spectrum of Rowland. The results given by MM. Eder and Valenta were obtained by photography. The intensities, *i*, are reckoned for 12= maximum.

The double line C α is generally given of the first importance; but its origin appears to be doubtful to MM. Eder and Valenta. On the other hand, several writers, using only a slight dispersion, have mistaken the least refrangible line of hydrogen, H α 657·3 (C of Frauenhofer), of which it is difficult to get rid, as one of its components. I therefore studied this part of the spectrum with most particular care, making use of a spectroscope with four prisms, on Thalén's principle, having great dispersive power. But whether with pure carbon or with melted carbonates, this instrument only enabled me to see one line, very well marked and slightly diffused, but not doubled. It corresponds very well to the most refrangible line of the so-called double one of Angström. I found for it a definite position, 657·85, taking as data H α 657·30 (Ames) and Li 670·82 (Kayser and Runge). The position of the three lines was measured in the same spectrum in turns and fractions of a turn of the micrometer screw of the apparatus. On the other hand, I have never been able to find the line 658·4 with pure carbon, in various pure and dry gaseous surroundings, or by varying the conditions of the experiment. I therefore consider it as not belonging to carbon.

Group I. is not very intense, but the line 537·99 and Group II. are strong and brilliant. The wide line in the indigo, C β 426·70, is the strongest and most characteristic of carbon. Increasing the condensation widens it enormously, even transforming it into a nebulous band.

All these lines have been observed, not only in alkaline carbonates, but in cyanides, sulphocyanides, and even in sulphocarbonates when below their temperatures of decomposition. I have even observed C α, C β, and Group II. by making a condenser spark strike between two solid beads of K_2CO_3 on two platinum wires.

Finally, I have observed in free carbon, in various gaseous media, a very well marked red line (609·70) the origin of which appears to be uncertain, for it is absent in the dissociation spectra of the carbonates, though its presence is incontestable in graphite, where no line foreign to carbon has yet been found.—*Bull. Soc. Chim.*, Series 3, vol. xix.-xx., No. 13.

Appointment.—Mr. E. H. Todd, a Matriculated Student at the South-Western Polytechnic Day College for Men, has been appointed to an open Exhibition in Physics and Chemistry at Christ Church, Oxford, of the value of £80 per annum, tenable for four years.

THE ESTIMATION OF BORIC ACID.

By M. VANDAM.

Klein has already studied the action of mannite on boric acid, and has noted the formation of a body giving an acid reaction with litmus paper; he also found an analogous property to this with glycerin, erythrite, dextrose, levulose, and the galactoses. Quercite and the polyglucocides behave in a different manner.

Lambert taking up the question, noticed that the property of forming acids in conjunction with boric acid belonged to the primary polyatomic alcohols.

Barthe proposed a method for the estimation of boric acid and borates, in which he made use of the associated acid body obtained by the addition of an excess of glycerin to the boric solution, and titrating with a solution of decinormal soda in the presence of sensitive litmus or phenolphthalein.

The number of c.c. of normal soda multiplied by 0·0062 gives by weight the amount of boric acid contained in the sample (0·0062 being the equivalent of BoO_3H_3),

In such an estimation I have substituted mannite for glycerin. With mannite the end of the reaction comes gradually, and the last drop of the titrated alkaline solution produces the blue colour perfectly and sharply; while with glycerin, even from the commencement of the operation, there is a persistent violet tint, the precise end of the reaction is more difficult to observe, and it is not at all easy to avoid making a noticeable error in two consecutive experiments.

For a long time past we have been successfully using this property of mannite in testing for and estimating boric acid in butters; we have made more than a hundred comparative examinations.

Testing for and Estimating Boric Acid in Butters.

1. Fifty grms. of butter are well washed with 20 c.c. of warm water.
2. The washings, nearly always acid, are saturated with a few drops of decinormal soda in the presence of sensitive litmus.
3. The blue liquid is divided into two test-tubes.
4. To one of these test-tubes we add 1 or 2 grms. of mannite, the other tube serves as a check.

In the presence of boric acid the tube containing mannite takes an intensely red colour.

With this solution we carry out the estimation by the use of decinormal soda, until the sudden appearance of the blue colour, when the number of c.c. of decinormal soda multiplied by 0·0062 will represent the weight of the boric acid contained in the sample.

The theory of these associated acid bodies is far from being clearly established. The following conclusions result from our researches:—

It is a fact that the addition of an excess of one of the polyatomic alcohols to a known weight of boric acid gives an acidity which is shown most distinctly by the aid of litmus, and that this acidity corresponds exactly to the volume of the decinormal solution of soda. Now, it seems evident that, since we can reciprocally substitute a hexatomic alcohol for a triatomic alcohol without interfering with the estimation as far as the calculations go, we estimate in this case, not the associated acid body, but only the boric acid taken progressively from its alcoholic combination by the soda of the titrated solution up to the moment when the polyatomic alcohol, completely free from its boric combination, remains inert, when the slightest excess of soda instantly produces the blue colour.—*Journ. de Pharm. et de Chim.*, Series 6, vol. viii., No. 3.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 3rd, 1898.

Professor Dewar, F.R.S., President, in the Chair.

(Concluded from p. 264).

129. "*The Yellow Colouring-matters of Rhus Cotinus and Rhus rhodanthema.* Part VI. By Arthur George Perkin.

Venetian sumach, the leaves of *R. Cotinus*, contains myricetin, and not quercetin as stated by Löwe (*Zeit. Anal. Chem.*, 1874, xii., 127). The leaves of *R. rhodanthema*, the yellow cedar of New South Wales, contain quercetin and gallotannic acid. The stems of both plants contain ficetin, and the leaves thus contain the more highly oxidised colouring-matters, as quercetin and myricetin are considered to be hydroxy- and dihydroxy-fisetin respectively. Other members of the *Rhus* family hitherto examined contain no fisetin in the stem. The Venetian sumach examined contained 16·7 per cent, and the *R. rhodanthema* leaves 9·5 per cent of tannin.

The leaves of *Artocarpus integrifolia* (Jackwood tree), *A. incisa* (bread fruit), and *A. lakoocha* are devoid of colouring-matter.

130. "*Colouring-matters of the New Zealand Dyewood 'Puriri.'*" By Arthur George Perkin.

"Puriri" (*Vitex littoralis*) is a large tree, growing in northern New Zealand, and chiefly used for building and similar purposes. Its tinctorial properties are little known. It contains two colouring-matters in the form of glucosides.

Vitexin, $C_{15}H_{14}O_7$ or $C_{17}H_{16}O_8$, the chief product, is a canary-yellow crystalline powder, distinguished by its sparing solubility in most solvents. Owing to the difficulty of obtaining substitution products without decomposition, its molecular weight is at present uncertain. *Acetylvitexin*, $C_{15}H_9O_7Ac_5$ or $C_{17}H_{10}O_8Ac_6$, forms colourless needles melting at 251—256°. On fusion with alkali, phloroglucinol, acetic and parahydroxybenzoic acids are formed, whilst boiling aqueous or alcoholic potash solutions give phloroglucinol and parahydroxyacetophenone. Further, the product of the ethylation of vitexin with boiling alcoholic potash yields paraethoxybenzaldehyde, paraethoxybenzoic acid, and a phloroglucinol derivative. Warm nitric acid (sp. gr, 1·54) forms metadinitroparahydroxybenzoic and picric acids, but when dilute acid is employed a sparingly soluble *nitro*-compound,—

$$C_{15}H_6O_5(NO_2)_4,$$

of unknown constitution, is also obtained in small quantity. This consists of small lemon-yellow needles, which dye mordanted calico; it is converted by strong nitric acid into picric acid, and appears to be closely related to vitexin. With nitrobenzene it forms an addition product, $C_{15}H_6O_5(NO_2)_4,C_6H_5NO_2$, crystallising in orange-coloured needles which lose nitrobenzene at 150°, or by digestion with alcohol. Vitexin gives very pure yellow shades on calico mordanted with chromium and aluminium salts, but owing to its insolubility these are of a poor character. They somewhat resemble the corresponding shades given by apigenin, and, as the chief decomposition products of both colouring-matters are identical, it is probable that apigenin and vitexin are closely related.

Homovitexin, $C_{16}H_{16}O_7$ or $C_{18}H_{18}O_8$, is present in the wood only in minute quantity. It crystallises in fine primrose-yellow needles, melts at 245—246°, and is distinguished from vitexin, which it otherwise resembles, by its ready solubility in alcohol. Fusion with alkali gives phloroglucinol and parahydroxybenzoic acid, and treatment with dilute nitric acid yields metadinitroparahydroxybenzoic acid. It dyes mordanted fabrics feebly.

The shades given by "puriri" with chromium and aluminium mordants are distinguished by their pure yellow tone, and may have some commercial utility.

131. "*Cannabinol.*" By T. B. Wood, M.A., W. T. N. Spivey, M.A., and T. H. Easterfield, M.A., Ph.D.

In former communications (*Proc.*, 1898, xiv., 66, 153) a number of derivatives of cannabinol have been described; a detailed account of these is given in the present paper. The oily lactone (*loc. cit.*, 153), prepared from nitrocannabinolactone (oxycannabin), is shown to be a metatolylbutyrolactone, oxycannabin being the corresponding nitro-derivative. By the oxidation of cannabinolactone, a lactonic acid is produced, which on fusion with potash yields isophthalic acid.

Nitrocannabinolactonic acid is obtained by oxidising oxycannabin either by dilute nitric acid in a sealed tube or by potassium permanganate.

The volatile fatty acids produced on oxidising cannabinol by nitric acid are shown to be normal butyric (Dunstan and Henry, *Proc.*, 1898, xiv., 44), normal valeric, and normal caproic acids, valeric acid being formed in the largest amount.

132. "*Derivatives of Hesperitin.*" By A. G. Perkin.

Hesperitin is found as the glucoside hesperidin in the citron, bitter orange, and other fruits of the same class. With potassium hydrate solution at 100° it gives phloroglucinol and hesperitinic or hydroxymethoxycinnamic acid. It thus appears to have the constitution—

$$OH{\cdot}C_6H_3(OMe){\cdot}CH:CH{\cdot}CO{\cdot}O{\cdot}C_6H_3(OH)_2$$

(Hoffmann, *Ber.*, 1876, ix., 685; Tiemann and Will, *Ber.*, 1881, xiv., 948). With alcoholic potassium and sodium acetates, hesperitin gives the compounds—

$$(C_{16}H_{14}O_6)_2,KC_2H_3O_2, \text{ and } (C_{16}H_{14}O_6)_2,NaC_2H_3O_2,$$

which form colourless needles and decompose on treatment with boiling water, regenerating hesperitin. With sodium and potassium bicarbonates, *sodium hesperitin*, $C_{32}H_{27}O_{12}Na$, and *potassium hesperitin*, $C_{32}H_{27}O_{12}K$, are obtained, crystallising in minute colourless plates. The formula of hesperitin is thus $C_{32}H_{28}O_{12}$.

Azobenzenehesperitin, $C_{32}H_{24}O_{12}(N_2Ph)_4$, forms red needles, melts at 246—247°, and yields a *diacetyl* derivative, $C_{32}H_{22}O_{12}Ac_2(N_2Ph)_4$, crystallising in ochre needles melting at 240—242°. Hesperitin should thus contain six hydroxyl groups, and this view of its constitution is confirmed by the formation of *acetylhesperitin*, $C_{32}H_{22}O_6Ac_6$, which crystallises in colourless needles melting at 127—129°.

If hesperitin were $C_{16}H_{14}O_6$, the constitution assigned by Tiemann and Will would thus be correct. Though not considered to be a polymeride of a substance of this formula, it must consist of two very similar groups linked together, as Hoffmann (*loc. cit.*) obtained from hesperitin a nearly quantitative yield of phloroglucinol and hesperitinic acid.

Research Fund.

A meeting of the Research Fund Committee will be held in December. Applications for grants, accompanied by full particulars, should be received by the Secretaries not later than December 5th. Forms of application can be obtained from the Assistant-Secretary, Chemical Society, Bualington House, W.

THE BANQUET TO PAST PRESIDENTS.

The Banquet to the Past Presidents who have been Fellows for half a century:—

	Elected.	President.
Gilbert, Sir Joseph Henry, F.R.S.	May 18, 1841 ..	1882-83
Frankland, Sir Edward, K.C.B., F.R.S.	December 20, 1847	1871-73
Odling, William, M.B., F.R.S.	January 17, 1848	1873-75
Abel, Sir Frederick Augustus, Bart., K.C.B., F.R.S.	March 21, 1848 ..	1875-77
Williamson, Alexander William, LL.D., F.R.S.	May 15, 1848 ..	1863 65 1869-71
Gladstone, John Hall, Ph.D., F.R.S...	December 18, 1848	1877-79

was held at the Whitehall Rooms, Hôtel Métropole, on Friday November 11th, 1898, Professor James Dewar, F.R.S., President, in the Chair.

After the toasts of the Queen and the Prince and Princess of Wales, the **President** said:—

"I have now the honour to propose to you what you must all regard as a toast to which I cannot possibly do justice, the health of six of the most distinguished Past Presidents of the Chemical Society who for more than half a century have been members of that body. It is admitted on all hands that Chemical Science has added enormously to the resources and power of mankind, and that its successful cultivation involves the exercise of every faculty of the human mind. We have here six illustrious examples of successful scientific culture, and, I would add, of bracing moral influence,—men whose one idea it has been, with steady aim and vigilant eye, to labour on with that sole incentive of scientific work, the triumphant hope of making an advance. These men have laboured for half a century in our interests, and they have added enormously to our knowledge of the science. It is almost impossible to realise the variety of the work they have done; the width of it is something appalling; when I tell you that, amongst them, they have recorded upwards of four hundred and fifty separate communications—how many there are that have not been recorded I cannot say—and that among these four hundred and fifty there are many papers of the highest importance, I am sure you will agree with me that they have exercised a remarkable influence on the development of our science. It was well that the Chemical Society of London—the oldest Chemical Society in the world—should inaugurate this banquet. The Council felt that probably they might never again have the opportunity of calling together such a distinguished body of men as they have the honour of offering this banquet to to-night. We are still able to go back to a man, who sits on my right hand, who worked in the laboratory of Thomas Thomson, who has seen Dalton and the beginning of the Atomic Theory, probably the most wonderful of all the laws of Nature which man has ever been permitted to decipher. That being the case, the way in which the idea has been received by all the chemists of this country is apparent from the number of men of talent and the variety of classes here to-night. But beyond that, the sympathy of every chemist in the world is with us to-night at this banquet. The large number of congratulatory telegrams and communications that we have received to-day from every country where the science of chemistry is cultivated, will give some idea of the appreciation with which this banquet is regarded throughout the whole civilised world. We have received communications from France, Holland, Belgium, Germany, Sweden, Russia, Austria, the United States, and other countries. It is unnecessary for me to read every name, for every man identified with the progress of chemistry in every civilised country has responded by sending some form of congratulation. In every case they write as if they were present with us, as you will understand from the few illustrations I will give you of the sympathetic language they use. Professor Friedel writes:—'I should have been happy to associate myself with the Chemical Society in doing honour to these veterans of science. I have the honour to be the friend of most of them, and the beneficent action they have exerted on Chemical Science cannot be esteemed too highly. They form the finest phalanx of the Fathers of our science which exists in any country. With these sentiments, you will understand the liveliness of my regret to be able to take part from afar and in spirit only in the honour paid them.' We have also received congratulations from learned societies both in Germany and Russia. At a meeting of the Russian Chemical Society the following resolution was passed:—'That the Society avail itself of the exceptional opportunity of being able to congratulate conjointly Sir Joseph Henry Gilbert, Sir Edward Frankland, Professor Odling, Sir F. A. Abel, Dr. A. W. Williamson, and Dr. J. H. Gladstone, whose distinguished services during half a century stand out as a model for all investigators in chemical science, and also express the wish to see the further results of their labours in the annals of science for many years to come.' The telegram from the German Chemical Society strikes me as very happy. Dr. Liebermann says:—'The sister Society sends both Jubilee congratulations and greetings to the Jubilee celebration of the Presidents of the Chemical Society, Gilbert, Frankland, Odling, Abel, Williamson, and Gladstone.' This shows, I think, that our Continental brethren appreciate the honour we desire to offer these distinguished men; and we need not be surprised that there is something more throughout these communications than mere cosmopolitanism in science. They breathe the spirit of friendly regard, of reverence, and even of love towards men who have done so much to advance the common cause of our science. How impossible it seems to sum up in any short speech the work that these men have done! If I attempted to classify them, I should say that if we regarded them as twos and twos they would not group well together, but if we take three at a time they bear somewhat close relations one towards another. I would say that Gilbert and Abel and Gladstone are monarchs of dependent kingdoms, whereas Frankland and Odling and Williamson are a triumvirate that have legislated towards the imperial side of chemical science.

"The work of Gilbert, as we know, was early differentiated into that most complex and mysterious study, the study of organic life. For the last fifty years he has devoted his attention to the physiology of plant life in every phase of its development. With a skill that has been unprecedented, he has recorded from year to year the variations in the growth of every kind of nutritious plant. He has examined into the meteorological conditions, the variations of climate, of soil and of mineral agents, of drainage, and of every conceivable thing affecting the production and development of plant growth. These memoirs are admitted throughout the world to be unique in their importance. Wherever the chemist or the physiologist, the statistician or the economist, has to deal with these problems, he must turn to the results of the Rothamsted experiments in order to understand the position of the science of our time. These results will be for ever memorable: they are unique and characteristic of the indomitable perseverance and energy of our venerated President, Sir Henry Gilbert.

"The next among them, Sir Edward Frankland, I should characterise as one of the most remarkable experimentalists of this or any other age. He has been gifted with an absolutely unique faculty for experimental work and observation. The breadth and variety of his work is positively astounding. From early times devoted to the study of Organic Chemistry, he has branched out not only into Mineral Chemistry, but every form almost of applied industry. His early work on the organo-metallic bodies, so fertile in the way of future development, will be ever memorable. These bodies have been the means of adding to our knowledge of synthetical substances produced in the laboratory in a way that no other agencies have operated. Along with this work, he has executed investigations bearing on flame and the character of the light emitted by various bodies, and on a large number of questions connected with sanitary chemistry. His great work on the water supply of the United Kingdom, on the sewage question, and other industrial problems, are generally acknowledged to be of great value and importance. Whatever work he has done is marked with the stamp of genius.

" The work of Odling has been an essential factor in the development of modern chemistry. It is characterised by precise and clear ideas, and an almost forensic ability for putting things in a straight, concise, and unembarrassing manner. His early labours in advancing the development of the newer chemistry deserve our warm gratitude, and his many published works and addresses on organic and inorganic chemistry, together with his translation of the work of Laurent, have all been of material service in diffusing a knowledge of our science. The papers he has contributed on Chemical Notation and on the question of types all display a marvellous precision as well as elegance of thought. Every one must admit the debt of gratitude we owe him for his iconoclastic labours in clearing out old and vague notions, and for the courageous manner in which he supported the newer ideas of his time.

" In the case of Abel, we have again a man who, at an early time, had his career differentiated for him. A distinguished student of Hofmann's, his early work was directed to organic chemistry, but he soon diverged into other channels, directing his attention to problems bearing on the chemistry of naval and military matters. We all know his splendid work on gunpowder, guncotton, detonation, and the whole field of explosive agents. Whether in connection with accidents in mines, from petroleum, or from flour, dust, or other agency, Abel has been a marvellous experimenter in the whole field of explosive chemistry. While engaged in these investigations in applied chemistry, however, he was adding to the advancement of pure science by the light which his researches threw upon many questions of chemical theory and by the stimulus thus given to further inquiry. He has had the great satisfaction of living through the age of gunpowder. That body had been the recognised explosive for many hundred years, and I have no doubt that when he commenced his investigations with Noble on gunpowder he never dreamt that he would live to see the day when he would clear out that smoky material and replace it before he left the War Office by a powder that is smokeless. I need hardly tell you that he has also added to our debt of gratitude by the personal services he has rendered to many learned societies.

I come now to Williamson. The work of Williamson proclaims him a truly philosophic chemist. He has had probably the greatest satisfaction of any one I know. He cleared up one of the most intricate and recondite of chemical reactions, that with which we are familiar as etherification, and in so doing he struck at the very root of the chemical problems connected with atomic and molecular weights, and realised and cleared up for ever those mysterious modes of explanation which were undoubtedly faulty and insecure. Before his time, men as great as Berzelius, Mitscherlich, and Graham, believed in that contact or catalytic action which in my early days bridged over the period between the old and the new, and was generally introdnced when no other explanation was forthcoming. Williamson cleared all that away; but the discovery of these ethereal nepenthes did not act in chemistry as they would have done physiologically; they did not produce a soporific effect. They struck at the foundations of our science, and it is to his great credit that he originated advanced ideas, not only as to etherification, but as to molecular weights, type formulæ, and so forth. In fact the chemistry of our time would not be the chemistry of our time but for the work of Williamson. I would further add that he was one of the earliest to introduce the idea of dynamics into chemical science. His suggestion of the dynamical theory of the voltaic battery and of dynamic mobility in apparent stability has been exceedingly fruitful since his time; and if we add to them that most important and original idea of Frankland's, the saturation power of the elementary bodies, we have all the agencies of our modern scientific notions. One other debt of gratitude we owe to Williamson, and that is the interest he took in introducing into this country abstracts of all the important scientific memoirs published on the Continent, It is to him we owe those valuable abstracts which have been printed for many years in the Chemical Society's *Journal*, and have done so much for the advancement of our science.

" Gladstone, on the other hand, represents a type somewhat different from that of any of the others that I have mentioned. He belongs to a characteristically English variety of men who have studied science for its own sake. Like Spottiswoode, De la Rue, and Joule, he has not been a professional scientist in the ordinary sense, but has worked out his long and brilliant scientific career as a labour of patient love. Furthermore, he has created an entirely new department—that which is in modern times regarded as physical chemistry, of which we have here to-night some distinguished representatives. For half a century he has worked on this side of chemistry, for his early investigation of the spectrum of the atmosphere was one of marvellous suggestiveness. He found that the spectrum of Fraünhofer varied at sunset and at sunrise from that at mid-day, and showed that a large number of those absorption lines must originate in the earth's atmosphere. That discovery stimulated further inquiry as to the substance that could produce these lines so characteristic of the solar atmosphere; and later experimenters have found it in the vapour of water and in oxygen. Gladstone's greatest merit, however, lies undoubtedly in his optical researches on the atomic refractions and dispersions of the elements. He has determined the optical constants of hundreds of bodies, and has thus stimulated inquiry in that borderland between physics and chemistry which is so much cultivated in the present day, and the pursuit of which has added so much to our knowledge. He has also contributed largely to miscellaneous inquiries, especially those connected with various voltaic batteries, and other questions conducive to the study of both organic and inorganic chemistry.

" This is but a brief epitome of the work of these great men. It would be, as I have said, hopeless for me to attempt to sum up all their individual labours. We can only skim the surface of the ocean of truth in which they have navigated so well and so successfully. But I will say this: that as experimentalists we are not likely to see their like again, and it is impossible to imagine a more extraordinary galaxy of chemical talent than these six Past-Presidents represent. They have rendered the science of chemistry more glorious for those who strive to follow; and the brilliant record of their discoveries can never be eliminated from the history of our Science. In the future, posterity will regard them as the most gifted and illustrious of the English chemists of the Victorian epoch. My Lords and Gentlemen,—I give you the health of our venerated Past-Presidents, Sir Henry Gilbert, Sir Edward Frankland, Professor Odling, Sir Frederick Abel, Professor Williamson, and Dr. Gladstone."

Sir J. HENRY GILBERT—" After the extremely flattering and eloquent terms in which our President has referred to the work of the six Past-Presidents of the Society who are so highly honoured to-night, it is surely a difficult task to say anything in response. I feel that any words of mine would be entirely inadequate; and I must, I think, fall back on what I was intending to say, and give a little personal history of the early times of the Society. You are aware, most of you, that I am to-night in the position of the senior of the Past-Presidents, in consequence of the death of Lord Playfair. He was, as you know, one of the founders of the Society, and, before he died, the only survivor of those founders. I myself came in within three months of the foundation, and so had some knowledge of the Society's early doings. In fact, before I was really admitted to the Society, under the influence of the late Professor Graham, I undertook the translation of a paper by Redtenbacher and Liebig on 'The Atomic Weight of Carbon'; and that paper occupies eighteen pages in the first volume of the Society's *Memoirs*. I should say that, less than a fortnight ago, I received a letter from Lady Playfair, just before she left to visit her friends in America, in which she said with what interest he had looked forward to being present at the banquet appointed for June—but that was not to be. I first made the acquaintance of Playfair in Liebig's laboratory at Giessen, the year before the establishment of this Society, that is, in 1840. Playfair was at that time very busily occupied in translating the memorable work of Liebig, 'Organic Chemistry in its Applications to Agriculture and Physiology'; and before the session was over he left for this country with Liebig, who was to present the substance of that work as a Report to the British Association at Glasgow in September. You may be interested to know who there were from this country in Liebig's laboratory at that time. Besides Playfair and myself, there were Dr. William Allen Miller, afterwards Professor of Chemistry at King's College; Dr. Stenhouse, who has contributed so much to the *Journal* of this Society; Dr. Angus Smith; and, lastly, Dr. Edward Schunck. He and I are, I believe, the only survivors of that time among those from England who were with Liebig then. Of the Germans who were there, some of the names you will probably remember. There were Heinrich Will, Varrentrapp, Redtenbacher, Hermann Kopp, Scherer, Bromeis, Boeckmann, and others of various nationalities; but I believe that not one of these survives at present. Schunck joined the Society early in 1842, and he from that time to this has devoted himself to scientific investigation. He built a laboratory, and a museum devoted especially to specimens of organic bodies, in his own grounds on the other side of Manchester, where he still lives. He was, in fact, the oldest member of the Society, I believe, except Playfair and myself. He has worked indefatigably ever since; but I am very sorry to say he is not able to be here to-night, having had an attack of bronchitis, which renders it impossible, though it would have given him great pleasure to be present. Referring to that time at Giessen, I may say that Playfair, Stenhouse, and myself, each took our degree then; and Playfair, though joining with us, having gone with Liebig, the responsibility was left with Stenhouse and myself to give the usual supper to the other students of the laboratory, and a few distinguished guests, among whom was Bunsen, who was then at Marburg; and who, I am glad to learn from Sir Henry Roscoe, is still well. Stenhouse was much my senior. We had a large and lively party, but Stenhouse did not enjoy that sort of thing very much, and when the last bottle of champagne was opened, he said: 'Now, Gilbert, I shall leave you to it,' and away he went. That was, however, not near the end of the evening. They stayed a very long time, and we did not exchange the smoky atmosphere of the supper-room for the clearer air outside until early morning. We then went round the boulevards of the little town, the Germans singing students' songs, and coming in time to the hotel where Stenhouse lodged, we serenaded him from the outside. Then someone tried the door, and finding it unfastened, the whole party went up, lighted candles, and serenaded him in bed. Next morning, there was a very capital caricature brought out, showing Stenhouse's rather long nose pointing in one direction, and his longer nightcap in the other. But this is enough of this kind of history, and I must now turn to rather more serious matters. It was in 1843 that I became associated with Mr. (now Sir John) Lawes, in agricultural investigation—a collaboration which has now extended over more than fifty-five years. As you all know, however rude may be some of the methods of the art of agriculture, the investigation of the principles underlying its practices involves a wide range of scientific inquiry. It involves the chemistry of the atmosphere, of the soil, of vegetation, and of animal life and growth. That is to say, besides chemistry, it involves meteorology, botany, vegetable physiology, and animal physiology, to some extent. It is impossible to be a specialist in so many subjects, particularly in these days, and I can only say that in venturing to deal with these other branches of science we have taken great care to avoid mistakes. The wide range of the investigations must be accepted as some explanation of the fact that we have not contributed more of the results to the Chemical Society. Many of them being connected largely with other branches of science, have been recorded in other than purely chemical journals; whilst those having a more directly practical bearing have been published in the *Journal of the Royal Agricultural Society*, or in other agricultural publications—the Rothamsted papers now numbering considerably more than one hundred. But we feel that, however long or short may be the time that we shall still work together, we shall perhaps have done as much in opening up as in solving problems; and that we shall certainly leave plenty for our successors to do. In conclusion, considering that there still remain five of your honoured guests to speak, this is all I will say of my own career, and I will only now ask you, Mr. President, the Council, and the Fellows of the Chemical Society, to believe that I esteem very highly the great honour you have conferred upon me to-night."

Sir Edward Frankland—"Allow me to thank you, Mr. President, and the Council of the Chemical Society for this delightful entertainment which you have prepared for the Past-Presidents who have attained Jubilee rank. It was a generous, unique, and happy idea, which I feel sure we all heartily appreciate, not only as we sit at your hospitable board, but also when we reflect on the kind feelings which led to the conception of that idea. There used to be a phrenological organ entitled 'love of approbation,' and whether there is or is not a part of the brain told off to perform this function, I trust that chemists are not behind the rest of humanity in appreciating such an honour as you have conferred upon us on this auspicious occasion. Nothing could he more agreeable than thus meeting so many colleagues who are worthily keeping up the high reputation of the Chemical Society. There is but one drawback to our enjoyment, and it has been very feelingly alluded to by Sir Henry Gilbert, namely, that one who so recently stood at the head of our Past-Presidents should not still be present amongst us. In the lamented death of Lord Playfair, chemistry and science generally have sustained an immeasurable loss; for he was a binding-link between science and the State, always ready to fight for the cause of truth against prejudice and ignorance, and never ceasing in his efforts to bring home to our rulers the vast importance of the applications of science to the progress, health, and prosperity of the nation. As one of his first pupils, and after a life-long friendship, I may be permitted to testify that his energy in this cause was prompted by sincere convictions and not by political exigencies. Had Playfair lived a few months longer, we should never have had the misfortune to make the acquaintance of that new variety of *Homo sapiens* the 'conscientious objector,' who is just now giving so much trouble to our magistrates. This is not a time to sketch, even in merest outline, the epoch-making work of the Society, but I may at least state my conviction that it will be found, on comparing the volumes of our *Transactions* with those of the corresponding societies of other lands, that, considering the number of workers in each case, England is not behind any other nation in research work, and this in spite of the almost total absence of that lavish state aid which nearly every other civilised nation enjoys. In view of the vast number of discoveries pouring out from chemical laboratories, I hear it suggested that the day is not far distant when there will be nothing left to discover, when all the elements in the cosmos shall have been captured and fitted into the Periodic System of Newlands and Mendeleeff, when there is not one more gas in the atmosphere left to be detected, and every element and group of elements shall have its ortho-, para-, and meta-position assigned to it. What will then remain to be done? Fortunately for investigators, we shall still be only as children gathering pebbles on the shore of the great ocean of knowledge. As yet we have only found the big boulders. To change the metaphor, chemistry now occupies the position of geography a century ago. The enormous number of chemical compounds are like so many islands, their latitude and longitude ascertained with precision, but on which the foot of man has not been put down, whilst their animals, plants, and minerals have never been exploited. When the ideal state of knowledge has been attained, chemists will perhaps find time to explore this vast archipelago, in which, there is no doubt, many interesting discoveries await those who shall undertake the task. Who can set a limit to the usefulness of these explorations? Even the most unpromising compounds may turn out valuable prizes! When aniline, chloroform, and carbolic acid were discovered, who could have predicted the revolutions in the arts and surgery which these bodies were destined to produce! They were but as desert islands until they attracted the attention of Hofmann, Perkin, James Simpson, and Lister. As chemists, I believe we have a noble future before us. Chemistry is distinguished from all other branches of knowledge as the helpmate of nearly every other science. The geologist, the botanist, and the physiologist find no thoroughfare unless they call in the help of the chemist. As soon as the physicist breaks into a molecule, he is trespassing on our domain. The bacteriologist has found that it is not the waggling of the tail of a pathogenic microbe that is the most important feature of its history, but that the chemical compounds which it secretes demand his closest attention. Even the astronomer has already to sit at the feet of the chemist! Thirty-three years ago, when our worthy President was but a youth, there was once a dinner party composed chiefly of chemists held at the Albion. A few are still living—among them being Sir F. Abel, Prof. Odling, and myself. In an after-dinner speech on that occasion, my friend Abel is reported to have expressed himself in blank verse as follows:—(I hope he will forgive me, at this distance of time, for appropriating his words to my own use).

"'Looking to right and to left, I see many faces around me,
Faces so old and familiar I feel once again at the College,
Testing, as in former times, for chlorine with nitrate of silver;
Gazing with youthful delight at crystals just hatched in a beaker,
Yearning o'er aniline drops distilling from crystal alembic.
O! my dear friends, one and all, we have toiled up a difficult pathway!
Some are low down on the hill, and others are near to the summit.
Let us remember the past and forget not our absent companions;
Fortune may come to us all; but youth will return to us never!'"

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, November 25th, 1898.

Mr. Shelford Bidwell, F.R.S., President, in the Chair.

Mr. R. A. Lehfeldt read a paper on "*The Properties of Liquid Mixtures*," being Part III. of his communications on that subject.

It deals with partiably Miscible Liquids. Measurements are given of the vapour-pressure of mixtures of phenol and water. This pair of liquids is completely miscible above 68° C., and incompletely miscible below that temperature. The law of equilibrium between incomplete mixtures and the vapours over them is investigated, especially at "the critical point," *i.e.*, at the point where incomplete miscibility passes over into complete miscibility. It is pointed out that normal organic liquids always mix completely. Ethylene dibromide and formic acid mix on boiling, and separate into two layers when cold. The curves representing the cases of complete mixture are comparable in shape with those previously obtained by Mr. Lehfeldt for mixtures of alcohol and toluene, but they show a still flatter maximum; so much so that 60 per cent to 70 per cent of phenol may be added to water without appreciable effect on the vapour-pressure. To verify this point a differential pressure-gauge was designed; the construction and method of using are given in the paper. The behaviour of the liquid is apparently the same above and below the critical point. At temperatures not too close to the critical point the vapour-pressure of a saturated mixture is approximately the sum of the partial pressures, calculated for the two saturated solutions according to Raoult's law. Diagrams are drawn showing the characteristic surface for phenol-water mixtures, with the freezing points of water and of phenol traced out. Phenol melts under water at 1·5° C., and forms a cryohydrate containing 4·83 per cent phenol, melting at −1·0° C.

Prof. S. Young (Abstract of Communication).—The statement of Mr. Lehfeldt that normal organic liquids always mix completely, should be qualified. There are pairs of normal organic liquids which, though miscible in all proportions, approximate closely to partially miscible liquids: *e.g.*, benzene (b. p. 80° C.) and normal hexane (b. p. 69° C.). When American petroleum is fractionally distilled, the benzene which is present in small quantity does not come over at about 80°, but mostly at about 65°; the most probable explanation appears to be that benzene and hexane behave, as regards distillation, like miscible liquids, a view which is confirmed by an investigation of the boiling-points, and also of the specific gravities of mixtures of the two hydrocarbons, an account of which has lately been read before the Chemical Society, by Messrs. Young and Jackson, The boiling-point curve is similar in general form to that of phenol and water, as shown by Mr. Lehfeldt, though the deviation from the ordinary form is not so marked. Ten per cent of benzine has practically no influence on the boiling-point of normal hexane, but 10 per cent of hexane lowers the boiling-point of benzine nearly 3° C. Also there is always expansion on mixing benzine and hexane, the maximum reaching about 0·4 per cent.

Dr. S. P. Thompson asked whether any relation had been observed between the vapour-pressure and the surface tension of the mixtures.

Mr. Lehfeldt was not sure whether the surface-tensions of the components pass into one another at the critical point of mixture.

Mr. L. N. G. Filon then gave an account of his paper on "*Certain Diffraction Fringes as Applied to Micrometric Observations.*"

It is to a great extent a critical investigation of a paper by A. A. Michelson on the same subject (*Phil. Mag.*, vol. xxx., pp. 1—21, July, 1890).

Michelson there describes a method for measuring the angular distance between the components of a double star, or the angular dimensions of very small celestial bodies, by means of interference-fringes, using two adjustable slits in front of the objective of a telescope. If the star is double, or if it has an appreciable disc, then by widening the distance between the slits, the fringes become fainter, and in some cases almost vanish. But by still further widening the slit, the fringes reappear, disappear, and so on. In the paper (*l.c.*) Michelson develops the law of these appearances and disappearances, and gives an expression for the ratio of the angular distance between the components of the double star, or the angular radius of the single source, to the distance between the slits, *on the assumption that the slits are infinitely long and infinitely thin.* Mr. Filon considers that this assumption is unjustified by the conditions of measurement; he reviews the original investigation, and modifies the results. He then proceeds to find equations to represent the intensity of light in the focal plane, for a point-source, and for a two-point source. These fringes are only visible over a certain rectangle, called "the rectangle of illumination" of the source. In the case of a two-point source, if the distance, perpendicular to the slits, between the geometrical images of the two points, is an integer-multiple of the distance between two fringes, the maxima of one system correspond with the maxima of the other, the fringes overlap, and their intensity is augmented. If, however, this distance should be an odd multiple of the half distance between the fringes, the maxima of one system correspond to the minima of the other, and if *the fringes that are superposed* are of similar intensity, the fringing is nearly obliterated, a result that agrees with Michelson's law. But it is now shown that for this phenomenon to occur (1) the rectangles of illumination of the two sources must overlap to a very large extent—this consideration was neglected by Michelson; and (2) the angular distance between the two stars, measured parallel and perpendicularly to the slits, must be less than a definite amount, depending upon the wave-length and the length and breadth of the slits. In astronomical cases, the second condition is generally satisfied. If the rectangles of illumination do not overlap they can be respectively distinguished, and thus the star can be resolved by direct observation. If, however, an accurate measurement of the distance between the components is required by Michelson's method, the rectangles must be made to overlap. The paper includes an investigation of a refractometer that Michelson (*l. c.*) proposed to use for increasing the effective aperture of a telescope; it is shown that Michelson's law is generally true for that instrument, but certain limitations are pointed out. Extended sources are next considered, and also the shape and size of the object. The paper concludes with the description of a method by means of which the ellipticity of a very small disc may be measured by these diffraction fringes in the special case where Michelson's law holds good.

In reply to a question from Professor S. P. Thompson, Mr. Filon said that the minimum breadth of slit with which he had found it practicable to work, using monochromatic light with his telescope, was about half a millimetre.

The President proposed votes of thanks, and the meeting adjourned until December 9th.

NOTICES OF BOOKS.

Chemistry for Schools. An Introduction to the Practical Study of Chemistry. By C. Haughton Gill, late Assistant Examiner in Chemistry at the University of London, and Teacher of Chemistry and Experimental Physics in University College School. Tenth Edition. Revised and Enlarged by D. Hamilton Jackson, Ph.D. (Heid.), Demonstrator of Chemistry, Univ. Coll., Bristol. London: Edward Stanford, 26 and 27, Cockspur Street, Charing Cross, S.W.

For a book of comparatively so small a size, a considerable amount of information has been introduced. That it has reached a tenth edition shows that it is appreciated, and this edition has been brought up to the present date of knowledge. There are plenty of illustrations, and each chapter concludes with a series of questions bearing upon the subject under discussion. Whenever possible, pains have been taken to impress a statement by detailing a simple experiment that the student can perform himself: this is not only of great value as a means of fixing a truth firmly in the mind, but carries with it the charm of experiment—a matter of considerable moment in connection with elementary schools. No doubt there are many cases where a few simple experiments successfully carried out have decided the course of a boy's life.

A list of apparatus and chemicals, with prices and dealers' addresses, is given at the end of the book: this will be of use to those living in the country.

Metrical Tables. By Sir Guilford L. Molesworth. Third Edition, Revised and Enlarged. London: E. and F. N. Spon, Ltd., 125, Strand. New York: Spon and Chamberlain, 12, Cortlandt Street.

The value of Molesworth's Pocket-book Tables is so well known that little need be said beyond announcing the publication of this third edition. Now that the metric system has become so extended, a handy pocket-book containing a collection of useful tables has become almost indispensable.

There is a good index, and, as it is bound in limp cloth and is only a quarter of an inch thick, it can be easily carried in the pocket.

The Organised Science Series. First Stage: Inorganic Chemistry (Practical). For the Elementary Examination of the Science and Art Department. By Frederick Beddow, D.Sc., Ph.D. London: W. B. Clive, University Correspondence College Press, 13, Bookseller's Row, Strand, W.C.

Although professedly an examination book, the author has endeavoured to present his instruction in a sound, practical, and systematic way. Chapter I., Introductory Experiments, commences rather abruptly, "How to Bore a Cork," and simple descriptions are given of such useful operations as cutting and bending glass tubes, mounting platinum wires for flame tests, making a wash-bottle, &c. Then follows a list of the characteristic properties of some common substances, leading up to some simple quantitative experiments, and a note on weighing and the use of a balance; finally, a chapter is devoted to systematic analysis.

Although the matter is necessarily rather condensed, and the style somewhat abrupt, it is evident that the author has his object, "practical instruction," well in hand, and to an intelligent student the book will prove of real value.

CORRESPONDENCE.

ETHERION.

To the Editor of the Chemical News.

Sir,—The above so-called new constituent of the atmosphere discovered by Professor Brush was the subject of an article in the Chemical News of November 4th (vol. lxxviii., p. 221) by Sir William Crookes, who pointed out the probability of it being simply a residue of water vapour, but suggested that when the complete paper came to hand more light might be thrown upon the subject.

The American periodical *Science* for October 14th contains a complete account of the investigation, and on examination it fully bears out Sir William Crookes's forecast. The paper is very lengthy, but the one solitary fact put forward is that powdered glass, sand, charcoal, &c., on heating give up a gas which, at greatly reduced pressures (between fifty-millionths of an atmosphere and zero, as indicated by a special form of gauge), *in the* *absence of a drying agent*, conducts heat better than hydrogen! Now this, as was pointed out, is precisely what one would expect to get if water vapour is present, and it seems to be meagre evidence upon which to base the tremendous assumptions which follow in the paper. It is conjectured that "etherion will be found to consist of three or more gases forming one or more periodic groups of new elements"; that "etherion will at least account for some of the phenomena at present attributed to the ether"; that "it may be the medium of propagation of Röntgen rays in the vacuum glass and air!"

The reasoning, too, in the paper strikes one as very strange, as in the following instances:—"A specimen of very fine white siliceous sand heated in vacuum . . . gave a considerable amount of the new gas." Glass that had been deprived of etherion was exposed in a thin layer to air and then found, on exhausting and heating, to yield it "as freely as at first." And another experiment is given in which "several days of high heating, with frequent exhaustion, failed to wholly deprive the pulverised glass of its new gas." "From this and other reasons" Professor Brush believes "the new gas resides *in*, and not simply on the surface of, glass!"

As an instance of the speculative part of the paper, the following extracts are amusing:—

A curve, *g h*, is given in the diagram (Chemical News, vol. lxxviii., p. 197) showing the conductivity of the gaseous residue between pressures of 43 millionths and 0·38 millionth of an atmosphere, and at this last pressure the conductivity was found to be twenty-seven times that of hydrogen under the same conditions. Another curve, *o p*, gave at *p*=0·12 millionth, a conductivity forty-two times that of hydrogen, and it is concluded as "reasonably certain" that, if the curve *e f* had been carried to as low a pressure as *o p* it would have shown a conductivity of at *least one hundred times that of hydrogen*. On this astonishing assumption, the following table of molecular weight, density, specific heat, &c., is constructed:—

Comparison of Gaseous Properties.

1. Gas.	2. Molecular wt.	3. Density, D.	4. Relative specific heat.	5. Relative molecular velocity, $\frac{1}{\sqrt{D}}$	6. Relative heat conductivity.
Etherion	?0·0002	?0·0001	6000·?	100·?	100·
Hydrogen	2·	1·	1·	1·	1·
Helium	4·	2·	?0·300	0·71	0·73
Carbon monoxide	27·8	13·9	0·072	0·27	0·33
Air	28·8	14·4	0·069	0·26	0·32
Carbon dioxide..	43·8	21·9	0·064	0·21	0·21

Later on in the paper it is pointed out that the values given are only intended to indicate the order of magnitudes expected to be found on further investigation; but one cannot help thinking that, until very much further investigation has been made, there will be no need either to modify our views of the ether, the Periodic Law, or even to burden ourselves with a still further host of "new constituents of the atmosphere."—I am, &c.,

Physicist.

THE GASES OF THE ATMOSPHERE.

To the Editor of the Chemical News.

Sir,—Your readers will, I suppose, hardly expect Professor Ramsay to reply to the letter of your correspondent, "Suum Cuique," who has again addressed you on the question of the respective shares of Lord Rayleigh and Professor Ramsay in the discovery and subsequent isolation and study of argon. This is a subject of which I believe most chemists will feel that we have heard enough, more especially as Lord Rayleigh has himself expressed in the clearest possible terms his own feeling in regard to Professor Ramsay's share in the investigation. On the occasion of the annual meeting of the Chemical Society in March, 1895, after receiving the Faraday Medal from the hands of the President, Lord Rayleigh is reported to have spoken as follows:—

"He said that in returning his thanks to the Society, he was somewhat embarrassed because he felt that there ought to be another standing at his side. It was true that his researches, to which the President had referred, upon the densities of gases had rendered it almost certain that a new gas of some sort was concerned and probable that the new gas was in the atmosphere. But from this point to the isolation and examination of argon was a long step, and the credit for it must be shared equally between Professor Ramsay and himself. In some quarters there had been a tendency to represent that antagonism existed between chemists and physicists in the matter, though such a thought never entered his mind. Professor Ramsay was a chemist by profession, while he himself had dabbled in chemistry from an early age, and had followed its development with a keen interest." (See *Trans. Chem. Soc.*, 1895, p. 1107).

In the same year the Davy Medal was awarded to Professor Ramsay by the Council of the Royal Society, of which Lord Rayleigh was then a member and an officer. In conformity with an unwritten but very salutary rule, officers of the Society are debarred from receiving medals or other awards under the control of the Council during their tenure of office. Lord Rayleigh had, however, been the recipient of the highest honour which the Chemical Society has it in its power to bestow, and it is fair to surmise that he concurred in the award of the Davy Medal to his coadjutor in this work. If Lord Rayleigh had been dissatisfied his colleagues on the Council were in a position to be aware of it, but no hint of such a feeling has ever escaped him, and the award was felt by everybody outside to be just.

Is "Suum Cuique" so much in the confidence of Lord Rayleigh that he can pretend to know what conversations occurred between him and the numerous chemists whom he consulted, or that he is in a position to say that the Cavendish experiment was not mentioned by more than one of them?

Professor Ramsay says that he directed Lord Rayleigh's attention to the Cavendish experiment, and because he says so I believe him, and shall continue to do so until, or unless, Lord Rayleigh states the contrary. This up to the present he has not done.

The writer of anonymous letters may escape the charge of vanity, but when his communications assume the character of those which bear the signature of "Suum Cuique" they are open to the more serious charge of malice.

This unknown champion will scarcely ask us to believe that he is authorised by Lord Rayleigh to defend his scientific character. Lord Rayleigh's name is honoured throughout the civilised world; his reputation does not require to be propped up by anonymous support, neither does it hang upon such slender threads as suggested in the successive letters of your correspondent.—I am, Sir, &c.,

William A. Tilden.

Royal College of Science, London,
Nov. 28th, 1898.

The Sugar in Orange-peel.—J. Flatau and H. Labbé.—While trying to isolate in a state of purity the odorous ether which exists in essence of orange, the authors noticed that it was always accompanied by a very small quantity of a substance easily soluble in water, and after treating a quantity of the peel in a certain manner they succeeded in isolating a substance presenting all the characteristics of a sugar. To identify this sugar they prepared its hydrazone by Emile Fischer's method, and finally decided that it was mannose.—*Bull. Soc. Chim. de Paris.*

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvii., No. 5, August 1, 1898.

Action of Pure Phosphoretted Hydrogen on Copper Sulphate.—E. Rubénvitch.—Previous investigators obtained a black precipitate by the action of phosphoretted hydrogen on copper sulphate, of an indefinite composition. The author investigates the subject thoroughly. He acts on a measured quantity of copper sulphate with phosphoretted hydrogen, then filters the precipitate, and washes with distilled water freed from air. All these operations take place in a vacuum. The copper phosphide is well defined and free from metallic copper; it corresponds to the formula $P_2Cu_5.H_2O$. Apparently the reaction takes place in two stages; two unstable phosphides being first formed, which, in the presence of the oxygen of the air, are transformed—one into metallic copper and phosphoric acid, and the other into a black compound containing oxygen. In the absence of all traces of oxygen, the reaction takes place according to the equation—

$$10CuSO_4+5PH_3+6H_2O= \\ =2P_2Cu_5.H_2O+PO_4.H_3+10H_2SO_4.$$

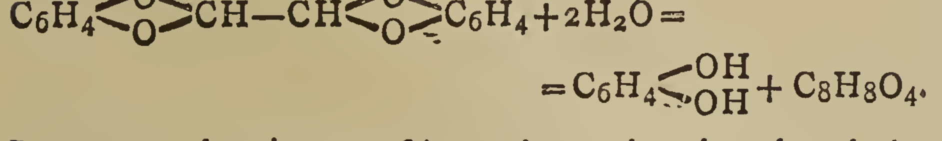
Copper phosphide dissolves in strong sulphuric acid with evolution of phosphoretted hydrogen. Nitric acid and bromine attack it easily, and it reduces permanganate of potash.

Action of Bromine on Normal Propyl Bromide in presence of Anhydrous Aluminium Bromide.—A. Mouneyrat. — The production of hexabromethane ($CBr_3—CBr_3$) by bromination with anhydrous $AlBr_3$ of ethyl bromide in successive stages has already been discussed. The present paper treats of the application of the same method to propyl bromide. Derivatives of propane were obtained with have hitherto been satisfactorily produced by no direct method. A solution of aluminium bromide in bromine was used; the given substance and the bromine being in theoretical proportions, corresponding to the general equation—

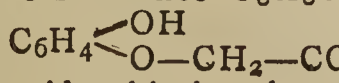
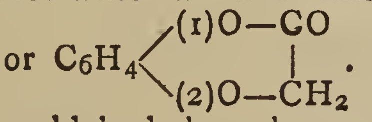
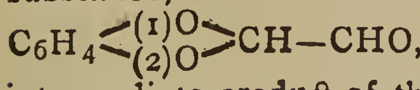
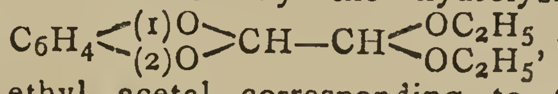
$$C_3H_xBr_y+Br_2=C_3H_{(x-1)}Br_{(y+1)}+HBr.$$

No. 6, August 8, 1898.

Hydrolysis of Ethane Dipyrocatechin.—M. Moureu. —In a previous publication, the hydrolysis of ethane dipyrocatechin by means of boiling dilute sulphuric acid has been discussed. The products are pyrocatechin and the substance $C_8H_8O_4$. Thus:—



$$C_6H_4{<}\begin{smallmatrix}O\\O\end{smallmatrix}{>}CH—CH{<}\begin{smallmatrix}O\\O\end{smallmatrix}{>}C_6H_4+2H_2O= \\ =C_6H_4{<}\begin{smallmatrix}OH\\OH\end{smallmatrix}+C_8H_8O_4.$$

By means of various reactions, the author has found the constitution of the substance $C_8H_8O_4$ to be represented by the formula  $C_6H_4{<}\begin{smallmatrix}OH\\O—CH_2—COOH\end{smallmatrix}$, viz., orthoxyphenyloxyacetic acid; this has been confirmed by synthesis. This body loses water when distilled, giving the anhydride, $C_8H_6O_3$, or  $C_6H_4{<}\begin{smallmatrix}(1)O—CO\\|\\(2)O—CH_2\end{smallmatrix}$. The latter substance, which is the aldehyd glyoxalmonopyrocatechin,  $C_6H_4{<}\begin{smallmatrix}(1)O\\(2)O\end{smallmatrix}{>}CH—CHO$, apparently constitutes the first intermediate product of the hydrolysis of ethane-dipyrocatechin, furnishing, by further hydrolysis, orthoxyphenyl-oxyacetic acid. That this surmise is correct is demonstrated by the hydrolysis of the compound  $C_6H_4{<}\begin{smallmatrix}(1)O\\(2)O\end{smallmatrix}{>}CH—CH{<}\begin{smallmatrix}OC_2H_5\\OC_2H_5\end{smallmatrix}$, which is simply the diethyl acetal corresponding to the above-mentioned aldehyd. The hydrolysis of this acetal was effected by Julius Hesse (*Comptes Rendus*, cxxvii., p. 276), and the product resembled in all respects the orthoxy-phenyl-oxyacetic acid of the author.

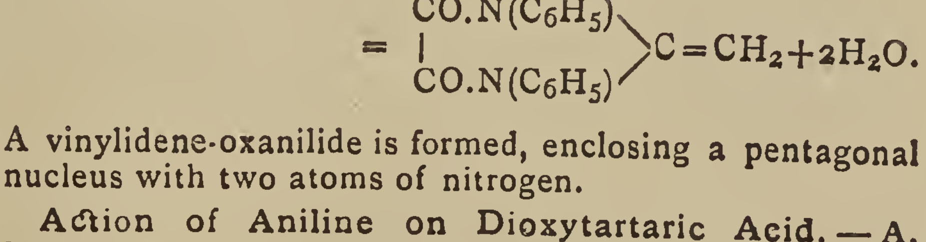
No. 7, August 15, 1898.

Atmospheric Carbonic Acid. — Albert Lévy and H. Henriet.—To collect the carbonic acid in the atmospheric air, the latter is allowed to bubble rapidly through a dilute solution of potash or baryta. The authors have investigated the amount present during the day, night, and at different times of year. They found—(1) that by their method all the free CO_2 was retained by the potash (this being proved by connecting a second potash tube on to the first, which did not vary in weight); (2) there was always less than half a litre of CO_2 to 100 m.c. of air; (3) that dilute solutions of various alkalis give exactly the same results; (4) that the variation in the amount of CO_2 in the air was very small during six years. If a globe of air which had been freed from CO_2 was left for some time in contact with potash, fresh CO_2 was formed. This showed that in the air there were carbonaceous substances, which in presence of oxygen and an alkali form CO_2. The amount of CO_2 formed was considerably more after the air had been left in contact with alkali for two hours than after ten minutes; but after two hours no increase in the amount was perceived, showing that the whole of the carbon was probably transformed into CO_2 in about two hours. The author gives tables of results for every day during three or four weeks.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xxxi., March 14, 1898.

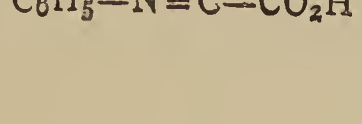
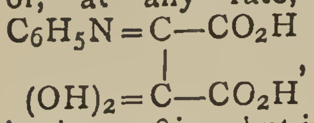
Formation of Metallic Sodium by means of Peroxide of Sodium.—H. Bamberger.—It is very easy to prepare metallic sodium as a lecture experiment by means of the peroxide. To effect this it suffices to heat the latter with charcoal, graphite, or coke in a covered crucible to about 300—400°. The reaction is rather violent and should only be performed on a few grms. at a time; most of the sodium is deposited on the cover and the sides of the crucible, $3Na_2O_2+2C=2Na_2CO_3+Na_2$. Peroxide of sodium reacts still more violently with carbide of calcium. If an excess of carbide be used, amorphous carbon is deposited, and a part of the carbide remains undecomposed. When the residue is decomposed by water, in the first case hydrogen is given off, and in the second case hydrogen and acetylene.

Action of Acetic Anhydride on the Anilides of the Bibasic Acids.—H. de Pechmann and W. Schmitz.—Oxanilide boiled for a long time with acetic anhydride and acetate of sodium reacts according to the equation—



$$\begin{matrix}CO.NH.C_6H_5\\|\\CO.NH.C_6H_5\end{matrix}+COOH.CH_3= \\ =\begin{matrix}CO.N(C_6H_5)\\|\\CO.N(C_6H_5)\end{matrix}{>}C=CH_2+2H_2O.$$

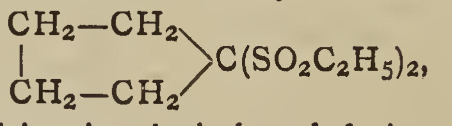
A vinylidene-oxanilide is formed, enclosing a pentagonal nucleus with two atoms of nitrogen.

Action of Aniline on Dioxytartaric Acid. — A. Reissert.—The author has endeavoured to prepare the unknown dianilsuccinic acid by the action of aniline on dioxytartaric acid,  $\begin{matrix}C_6H_5—N=C—CO_2H\\|\\C_6H_5—N=C—CO_2H\end{matrix}$. This body, or, at any rate, the monoanilidoxysuccinic acid, 

$$\begin{array}{l} C_6H_5N=C—CO_2H \\ \quad\quad\quad\;\; | \\ (OH)_2=C—CO_2H \end{array}$$

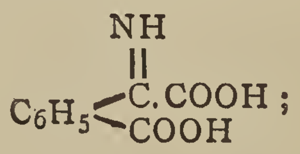
, seems to be the first product formed in the reaction, but it decomposes so rapidly that it cannot be isolated. When dioxytartaric acid is added to hydrochlorate of aniline, CO_2 is given off, and, according to the proportion of the base present, we obtain salts of aniline, anilidomalonic acid, or anilidomalonanilic acid. Anilidomalonic acid, $C_9H_9NO_4$, crystallises in white needles fusible at 121°, easily soluble in warm water and alcohol, less soluble in ether, and difficultly so in benzene and ligroïn. The free acid and the ammonia salt take an intense brownish red colour with Fe_2Cl_6. Anilidomalonanilic acid, $C_{15}H_{14}N_2O_3$, takes the form of microscopic needles fusible at 157°, decomposing into aniline and CO_2. It is soluble in the alkalis and the alkaline carbonates, insoluble in water and the organic solvents, it gives a yellow colour with Fe_2Cl_6, and is easily transformed into the preceding acid.

Dinitrodibenzoyldisulphonic Acid. (II.).—C. Ris and C. Simon.—The authors add several details on the method of preparing pure dinitrodibenzoyldisulphonic acid, and confirm the observations of Green and Wahl, according to whom the sodium salt of this acid, when pure, does not give a coloration with soda-lye and phenylhydrazin. When this salt of sodium is treated with hydrochloric acid, we obtain an acid salt and not a free acid. The analysis of the neutral sodium salt gives a result which does not correspond with its supposed constitution, but to a compound containing one atom of oxygen less. The percentage composition is that of a nitroso-nitrated derivative, but its constitution has yet to be determined.

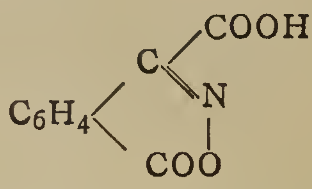
Sulphonals of Cyclic Ketones.—O. Wallach and W. Borsche.—The authors, taking into consideration the tendency of the cyclic ketones—in the same manner as acetone—to give products of condensation, have prepared the sulphonates of several cyclic ketones. Into a mixture of one molecule of pentanone and two molecules of ethylmercaptan, kept at the temperature of melting ice, they passed dry hydrochloric acid gas until saturation, and then oxidised the product formed; they obtained the sulphonal of pentanone, 

, insoluble in water, crystallising in alcohol and fusing at 127—128°. In the same manner, the sulphonal of methylpentanone, crystallising in prisms and melting at 110·5—111·5° was obtained; also the sulphonal of methylhexanone, difficultly soluble in cold water, melting at 104—105°; and the sulphonal of heptanone crystallising in absolute alcohol in prisms, and melting at 136—138°.

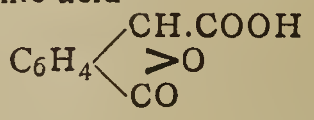
Phthalonic Acid.—C. Graebe and F. Trümpy.—Phthalonic acid forms an excellent substance to use for the preparation of a series of derivatives such as phthalaldehydic acid, phthalide, homophthalic, hydrodiphthallactonic, and β-desoxybenzoïn-carbonic acids. Phthalonic acid crystallises with 2 aq, which it loses slowly at 80—100°, and more rapidly at 110—120°; the anhydrous acid melts at 144·5°. When heated it forms, not only phthalic acid, but also phthalaldehydic acid, which becomes transformed into its anhydride and biphthalyle. Phthalonic acid evaporated on the water-bath with an excess of ammonia gives an acid with the probable constitution—



this acid, slightly soluble in water, dissolves easily in alcohol, giving an intense yellow colour. Hydroxylamine gives, with phthalonic acid, an oxime,—

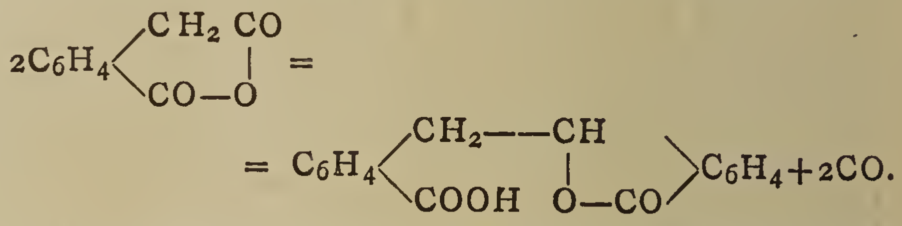


or a phthalimide according to the conditions. Treated with sodium amalgam, phthalonic acid becomes changed into phthalidcarbonic acid—



This can also be obtained by reduction in an acid solution by means of zinc powder or magnesium.

Homophthalic Acid.—C. Graebe and F. Trümpy.—The authors have prepared homophthalic acid by heating 10 grms. of phthalonic acid with 2 grms. of red phosphorus and 12 c.c. of HI of density 1·67 and 3 c.c. of water, for three or four hours, with a vertical condenser attached. When heated to about 190° this body becomes anhydrous; when further heated to 210—230° it forms hydrodiphthallactonic acid almost quantitatively:—



They have also prepared β-desoxybenzoïn-carbonic acid, which changes into isobenzal phthalide when heated to 200°.

Action of Diethyloxalic Ether on *p*-Amidophenol and its Ether.—A. Piutti and R. Piccoli.—A controversial paper not suitable for abstraction.

The Derivatives of Benzalacetophenone containing Nitrogen.—J, Tambor and F. Wildi.—The authors find that benzalacetophenone reacts with ammonia and the primary aromatic amines, while up to the present time the secondary aromatic bases, pure and mixed, have resisted this reaction, which is generally carried out in the cold, and as a rule with the absence of alkali. The products of condensation are generally white, but if, however, they contain a chromophore group, such as NO_2 for example, they become yellow or red. The authors have prepared dibenzalacetophenoneamine by condensing the benzalacetophenone with ammonia in alcoholic solution, and dibenzalacetophenone-nitrotoluidine, as well as the corresponding derivatives of the three isomerous nitranilines and of α-naphthylamine.

MEETINGS FOR THE WEEK.

MONDAY, 5th.—Society of Arts, 8, (Cantor Lectures). "Acetylene," by Prof. Vivian B. Lewes.

—— Society of Chemical Industry, 8. "On Oxone and its Commercial Applications," by Colonel W. J. Engledue, R.E. "An Improved Apparatus for the Estimation of Carbonic Acid in Minerals, &c.," and "The Preparation of Standard Solutions of Sulphuric Acid," by Arthur Marshall.

—— Royal Institution, 5. General Monthly Meeting.

TUESDAY, 6th.—"The Yangtse Basin and the British Empire," by Archibald Little, F.R.G.S.

WEDNESDAY, 7th.—Society of Arts, 8. "Egypt and the Soudan in 1897 and 1898," by W. T. Maud.

FRIDAY, 9th.—Physical, 5. "Longitudinal Vibrations in Solid Hollow Cylinders," By C. Chree, Sc.D., F.R.S., &c. "Thermal Properties of Normal Pentane," by J. Rose-Innes, M.A., B.Sc., and Sydney Young, D.Sc., F.R.S.

THE CHEMICAL NEWS.

Vol. LXXVIII., No. 2037.

ON THE

CONDENSATION NUCLEI PRODUCED IN GASES BY THE ACTION OF RÖNTGEN RAYS, URANIUM RAYS, ULTRA-VIOLET LIGHT, AND OTHER AGENTS.*

By C. T. R. WILSON, M.A.,
Clerk-Maxwell Student in the University of Cambridge.

The experiments here described consist mainly in determinations of the least degree of supersaturation necessary to cause water vapour to condense on nuclei from various sources.

As in former experiments (*Phil. Trans.*, A., 1897, vol. clxxxix., p. 265; *Camb. Phil. Soc. Proc.*, 1897, vol. ix., p. 333) the supersaturation is brought about by very sudden expansion of air or other gas originally saturated with water vapour, the expansion required to produce a fog or shower of drops being measured. The expansion is expressed in terms of v_2/v_1, the ratio of the final to the initial volume.

The following classes of nuclei have been studied in this way:—

1. Nuclei produced by Röntgen rays.
2. ,, ,, uranium rays.
3. ,, ,, ultra-violet light.
4. ,, ,, sunlight.
5. ,, ,, metals in contact with the gas.
6. ,, ,, the action of ultra-violet light on a negatively electrified zinc plate.
7. ,, ,, the discharge of electricity from a pointed platinum wire.

In addition the behaviour of the nuclei in an electric field has been studied, with the object of distinguishing between "ions" and nuclei which carry no charge of electricity.

1. The action of strong X rays on the gas differs from that of weak rays (*Phil. Trans.*, *loc. cit.*) merely in the number of nuclei produced, the supersaturation required to cause water to condense on the nuclei remaining unaltered. The value of v_2/v_1 corresponding to this degree of supersaturation (approximately fourfold) is equal to 1·25.

2. Uranium compounds, whether inside the expansion apparatus in immediate contact with the gas or contained in a glass bulb outside the apparatus (*Camb. Phil. Soc. Proc.*, *loc. cit.*), produce nuclei requiring the same degree of supersaturation as those produced by X rays.

(Expansion experiments probably furnish one of the most delicate methods of detecting these rays).

3. Ultra-violet light acting on moist air or oxygen produces nuclei which, when the radiation is weak, require quite as great a degree of supersaturation to cause water to condense on them as those produced by X rays. With stronger radiation, however, the nuclei appear to grow, the expansion required to produce a cloud now depending on the strength of the radiation and on the time for which the gas has been exposed to the rays before expansion. With very strong ultra-violet light the growth of the nuclei, even in unsaturated air, continues till they become visible, as stated in a preliminary note (*Camb. Phil. Soc. Proc.*, 1898, vol. ix., p. 392). The phenomena are then like those observed by Tyndall with certain vapours exposed to ordinary light. That nuclei are produced when ultra-violet light enters an expansion apparatus through a quartz window was discovered by Lenard and Wolff, but they believed them to arise from disintegration of the quartz. That these nuclei arise not at the quartz, but throughout the volume of the air exposed to the rays, is capable of experimental proof in a variety of ways. In hydrogen even strong ultra-violet light produces comparatively few nuclei, these requiring also as great a degree of supersaturation as the nuclei produced by X rays in order that water may condense on them.

4. Sunlight produces in air nuclei which require large expansions (v_2/v_1 about 1·25) in order that water may condense on them.

5. Certain metals in moist air produce nuclei, always requiring great supersaturation in order that condensation may take place on them. The supersaturation required is generally as great or greater than that required in the case of X ray nuclei. In the presence of amalgamated zinc dense fogs are obtained with expansions, which in the absence of the metal only result in the formation of a very few drops. Clean surfaces of zinc or lead have a similar but much slighter effect; with copper or tin it is inappreciable. These phenomena are obviously closely connected with the effects which these metals exert on a photographic plate, studied by Russell and others.

6. Ultra-violet light acting on a negatively electrified zinc plate produces condensation nuclei, as was proved by the steam jet experiments of Lenard and Wolff. The nuclei, however, are not, as these observers supposed, produced by disintegration of the metal, for expansion experiments show that they are identical with the nuclei produced by X rays with respect to the degree of supersaturation required to cause condensation to take place on them, and therefore entirely unlike dust particles. In hydrogen the maximum number of drops in the fogs which result on expansion is obtained with comparatively weak fields; no nuclei are produced when the zinc is positively electrified.

7. The discharge from a pointed platinum wire in moist air or hydrogen produces nuclei which also require approximately the same expansion, $v_2/v_1 = 1{\cdot}25$, in order that condensation may take place on them. If the expansion be made while the discharge is taking place no fog is obtained with smaller expansions. The results are not so simple if the expansion be made after the discharge has ceased, apparently on account of some secondary effect of the discharge causing the nuclei to grow. No nuclei were produced unless a glow could be observed at the point of the wire.

Effect of an Electric Field.—When air exposed to X rays is enclosed by two parallel plates, between which a sufficient difference of potential is maintained, the fogs obtained on expansion are very much less dense than in the absence of the electric field, and if the rays be turned off before expansion all the nuclei are found to have been removed, whereas without any electric field a fog is obtained even if the expansion be not made till some seconds after the rays have been cut off. This behaviour of the nuclei proves them to be charged particles or "ions." The nuclei produced by uranium rays behave in a similar manner; those produced by the action of ultra-violet light on moist air, or by the presence of metals, are entirely unaffected by an electric field. They are therefore not ions but uncharged nuclei. (Since the nuclei produced by the action of metals on air or by weak ultra-violet light require just as great a degree of supersaturation as those produced by X rays to cause water to condense on them, the difference in the behaviour of the two classes of nuclei can scarcely be due to a difference in size). The nuclei which escape from a negatively electrified plate under the influence of ultra-violet light are of course charged.

It follows from the experimental results described in this paper that the passage of electricity through gases is effected by charged particles which have an identical effect as condensation nuclei, whether the conduction is the re-

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* Abstract of a Paper read before the Royal Society, November 24, 1898.

sult of exposure of the gas to X rays or uranium rays, or of the action of ultra-violet light on a negatively charged zinc plate, or consists in the escape of electricity from a pointed platinum wire. In all cases the degree of supersaturation required to make condensation take place on these particles is approximately fourfold (*Phil. Trans.*, *loc. cit.*).

The nuclei which are produced and grow (in air or oxygen under the action of ultra-violet light are uncharged, in their initial stages at least; they are therefore not electrified water drops. It is possible that they are water drops containing in solution some substance, perhaps H_2O_2, produced within them by the action of the ultra-violet light in quantities sufficient to counterbalance the effect of the curvature of the surface upon the vapour pressure necessary for equilibrium.

EXAMINATION AND SEPARATION OF THE EARTHS OF MAGNESIA, AND OF OXIDE OF MANGANESE, IN THE PRESENCE OF ACIDS FORMING INSOLUBLE SALTS WITH THESE BODIES.

By M. A. VILLIERS.

In the qualitative examination of bases the precipitate obtained by adding an excess of ammonia to the solution resulting from a previous treatment by sulphuretted hydrogen after peroxidation of the iron, and in presence of hydrochlorate of ammonia, may, as is well known, have a more or less complex composition. In the absence of acids which form insoluble salts with these bases, such as lime, it cannot contain any other metals besides iron, chromium, and aluminium. In the contrary case it may contain a part or the whole of the lime, baryta, strontia, manganese, and magnesia.*

In all analytical treatises one is obliged to give two methods to be followed in the study of the ammoniated precipitate, according as we have to deal with one or other of these cases. Besides this inconvenience, the examination of the eight metals which may enter into the composition of this precipitate is always long and delicate. Further, we have to test for and separate the lime, baryta, strontia, manganese, and magnesia, twice,—in the ammoniacal precipitate and in the filtered liquid.

It is easy to avoid these inconveniences and to obtain —no matter what the original solution may be—a precipitate containing only the three sesquioxides.

Let us first see which are the acids whose presence may cause the precipitation by ammonia of other bases than the three sesquioxides.

We first eliminate silicic acid, which is easily separated by evaporation to dryness, after the addition of hydrochloric acid.

In the same manner the solution, after treatment with sulphuretted hydrogen, should be freed from carbonisable organic acids, such as tartaric and citric acids, whose presence would prevent the precipitation of the sesquioxides.

There is no need to try and separate boric acid. The borates are too soluble in the presence of ammoniacal salts to make it necessary to test for them in the washed precipitates.

There therefore remain oxalic acid and phosphoric acid. We shall show later on how easily the first can be destroyed and the second separated. It is in an acetic solution and in the state of ferric phosphate that we can effect this separation. This well-known method for the elimination of phosphoric acid does not appear up to the present to have given results of indisputable accuracy in the separation of this acid and the alkalies. It can, however, be adapted to the qualitative and quantitative separation of phosphoric acid, as well as of lime, baryta, strontia, manganese, and magnesia, and further this separation is as complete as in the case of the alkalies, if carried out under favourable conditions.

Although the earthy phosphates and phosphate of manganese are soluble in acetic acid, it is not sufficient that the acetic solution should contain a quantity of ferric salt theoretically sufficient for the precipitation of the phosphoric acid, or that it should be added. We have noticed, in fact, that even with solutions containing a notable excess of iron, the precipitate obtained by boiling after the decomposition of the acetate of iron, separated by filtration from the solution freed from phosphoric acid, after thorough washing, may contain a large proportion of the earthy metals and of manganese. This entanglement is probably due to the formation of double salts, insoluble in acetic acid.

In the same way if—to an acid liquor containing a ferric salt and a base such as lime in the presence of phosphoric acid—we add an excess of ammonia, the precipitate thus obtained treated with acetic acid will give up none, or only a part, of the lime it contains, and that even when the iron is in excess with regard to the phosphoric acid. And again, freshly formed phosphate of iron, added to a solution of the chloride of the earthy metals, retains a large proportion of these latter when the solution is made alkaline with ammonia.

Phosphoric acid cannot be completely separated in the state of ferric phosphate from the earths and from manganese in acetic solution, except when we have a very large excess of iron in proportion to the phosphoric acid present. We shall see below how to make quite certain that this excess is sufficient. We will now describe the method to be followed for the separation of the three sesquioxides from the following metals :—

Experiments on Fe, Cr, Al, Ca, Ba, Sr, Mg, Mn, in the presence of Acids forming Insoluble Salts with these Metals.

If necessary the organic matter is first destroyed by calcination. The silica is eliminated by evaporation to dryness in the presence of hydrochloric acid.

Phosphoric acid is tested for in a small portion of the solution by means of molybdate of ammonia.

Oxalic acid is also tested for :—

1. In the presence of phosphoric acid: if a test on a small portion indicates the presence of manganese, the presence of oxalic acid will be manifested by a disengagement of CO_2, making the solution cloudy with baryta, at the moment when the liquor resulting from the treatment with sulphuretted hydrogen, after acidulating with hydrochloric acid, is peroxidised with nitric acid. If no manganese is present we add a few drops of chloride or of nitrate of this metal to a portion of the solution, and make the same test.

2. In the absence of phosphoric acid we test for oxalic acid by means of a *salt of lime* and *acetate of soda*.

If oxalic acid is found to be present it must be destroyed in the whole of the solution, either by calcination (it cannot be present if we have already destroyed the carbonisable organic matters) or by the action of hydrochloric and nitric acids and of a salt of manganese, prolonged until CO_2 is no longer given off. If the solution does not contain a manganese salt, and it has to be added, account must be kept of the amount added in the subsequent results.

In the absence of phosphoric acid the testing for bases is conducted in the ordinary manner, and the sesquioxides are precipitated by ammonia.

If phosphoric acid is present it must be removed, after peroxidation of the iron, in the state of ferric phosphate,

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* As for the zinc, cobalt, and nickel, it is quite a mistake to include them in certain analytical tables; they do not form permanent precipitates, insoluble in excess of ammonia, even in the presence of acids forming insoluble salts; always on one condition, and that is—that enough ammonia or ammonia salts has been added

at the same time as the three sesquioxides are separated. We partially neutralise by adding ammonia, drop by drop, until the precipitate commences to appear; re-dissolve the precipitate in the smallest possible quantity of hydrochloric adid, then add a *small quantity* of an *alkaline acetate*.

If the iron is in great excess this addition will not cause precipitation in the cold, on account of the solubility of ferric phosphate in the ferric salts. If, on the other hand, a precipitate is formed, we add a small quantity of *perchloride of iron* (iron has been found by a previous test), and we wait a few instants to see if the solution becomes limpid again. If necessary fresh quantities of perchloride of iron are added, to obtain complete solution, and this is verified by the addition of a drop of an alkaline acetate, which should not produce a precipitate; if it does, more acetate and perchloride of iron must be added.

It only now remains to dilute with water if the colour is very intense, and boil for some instants. If the solution remains coloured, acetate must be gradually added until the colour disappears. Filter while boiling. (If this operation takes much time, traces of iron may be redissolved, thanks to the carbonic acid in the air; this is removed by boiling the filtrate and passing it through a second filter.

The solution is re-heated with a slight excess of ammonia; if a further precipitate of sesquioxides is formed, it must be collected on another filter and added to the preceding one.

In the precipitate the sesquioxides are found; and in the solution concentrated by evaporation, the bases comprising the earths and the manganese, in the ordinary manner.

We may remark that the separation of the manganese from the sesquioxides, being made here in acid solution, is much more distinct than when these latter are precipitated by ammonia; for in the latter case it is almost impossible to prevent, during the filtration and washing, the action of the air on the liquid, with the precipitation of a small part of the saline oxide of manganese which will be thus found mixed with the precipitate.—*Bull. Soc. Chim.*, Series 3, vol. xix.-xx., No. 15.

NOTE ON

A TUNGSTO-POTASSIC TUNGSTATE, AND A NEW METHOD OF PREPARING BINOXIDE OF TUNGSTEN.

By **L. A. HALLOPEAU.**

By submitting acid tungstate of soda heated to redness to the action of hydrogen, Wöhler obtained cubical crystals possessing the colour and brilliancy of metallic gold; he considered this compound to be a bitungstite of sodium, $Na_2O.2WO_2$, but some years later Malaguti showed that this formula was incorrect, and that the compound in question was what he called a *tungstate of sodium and of tungsten*, with the formula $Na_2O.WO_3+WO_2.WO_3$.

Shortly afterwards Laurent prepared, by Wöhler's method, a body by the reduction of tungstate of potassium, which he obtained in small needles of a deep coppery violet-red colour, resembling sublimed indigo; but he gave no indication as to the probable composition of this body, which he did not analyse. I therefore decided to examine carefully the action of acid tungstate of potassium.

The paratungstate of potassium which I used was placed in a small porcelain boat in a glass combustion-tube, through which a slow current of hydrogen was passed, at the same time heating to as high a temperature as possible,—in fact, almost to the fusing-point of the glass. The experiment should last about three-quarters of an hour. On breaking the glass tube after cooling, we find in the boat a violet-coloured substance, appearing reddish by reflected light; this is treated successively with boiling water, cold concentrated hydrochloric acid, and a boiling 50 per cent solution of carbonate of potassium, after which it is again washed with hot water. All these washings should be prolonged so that the purification may be complete. This substance occurs in small prisms of a violet-red colour, with a coppery appearance by reflected light; when examined under the microscope these prisms appear to resemble crystals of permanganate of potassium. They certainly seem to be identical with the needles described by Laurent. Their composition corresponds to that of the compound of soda obtained by Wöhler; according to my analyses the formula is—

$$K_2O,WO_3+WO_2,WO_3.$$

	Found.		Calculated.
	I.	II.	
K_2O ..	12·37	11·51	12·14
3W ..	71·36	71·95	71·32
8O ..	—	—	16·54
			100·00

When paratungstate of potassium was submitted to the action of hydrogen at a much lower temperature (dull red) I obtained a mixture of the above-mentioned body, together with a large quantity of binoxide of tungsten and of the blue oxide of tungsten; under these conditions the purification of the product is very difficult.

Finally, by heating the paratungstate of potassium in hydrogen to a bright red heat in a porcelain tube, I found nothing in the boats but very brilliant metallic tungsten. This method of preparing metallic tungsten forms the best means for obtaining it in small quantities.

The results of these experiments show that when we heat paratungstate of potassium in hydrogen, we obtain first, at a low temperature, the blue oxide and the binoxide of tungsten. At a higher temperature *tungsten bronze*, $K_2O.WO_3+WO_2.WO_3$, is formed; it is easy enough to obtain only this compound if we operate at exactly the right temperature. Finally, at a bright red heat, this tungsten bronze is in its turn reduced, giving metallic tungsten.

The action of hydrogen on paratungstate of lithium gave me a different result. Paratungstate of lithium was also distributed in porcelain boats placed in a glass tube and heated in hydrogen for three-quarters of an hour at a temperature approaching the melting-point of glass. After cooling there remained in the boats a brown substance, which was treated successively with boiling water, concentrated hydrochloric acid, and a boiling 20 per cent solution of lithia; the product was then carefully washed with warm water.

In this manner we obtain a brown powder having a metallic coppery appearance by reflected light, composed of very small and completely opaque crystals; under the microscope these crystals have the appearance of octahedra. This is *binoxide of tungsten*; its formula is WO_2.

	Found.		Calculated.
	I.	II.	
W ..	85·35	85·37	85·19
O_2 ..	—	—	14·81
			100·00

This method enables us to prepare rapidly large quantites of binoxide of tungsten; the paratungstate of lithium which is used contains 94·89 per cent of tungstic acid. Further, the reduction of paratungstate of lithium by hydrogen gives a pure brown binoxide of tungsten, which is difficult to obtain by reducing tungstic acid in a current of hydrogen at a dull red heat, as is generally done.

By this latter process we do not always obtain a product of a constant composition, for, according to the temperature and the duration of the reaction, the reduction may be incomplete, or there may, on the contrary, be a small quantity of metallic tungsten formed.

Binoxide of tungsten prepared by the reduction of paratungstate of lithium is not attacked by hydrochloric acid, or by concentrated alkaline solutions, either hot or cold; we thus see that in the preparation of tungsten bronzes with a potash or soda base, it is absolutely necessary to prevent the formation of this binoxide by working under suitable conditions of temperature.

Paratungstate of lithium, which serves as the primary material for the performance of this operation, is obtained by dissolving tungstic acid in a warm solution of carbonate of lithium, and adding hydrochloric acid until the reaction is slightly acid. On evaporation the solution deposits voluminous plates or rhomboidal prisms, which may be purified by further crystallisation. The extreme solubility and the great deliquescence of these crystals is at first a cause of difficulty, but they can be easily separated from the mother-liquor by using a conical funnel recently invented by M. Tassilly, for drying in a closed vessel bodies which are liable to decomposition by air.—*Bull. Soc. Chim*, 1898, Series 3, vol. xix.-xx., No. 16-17.

THE SPECTRUM ANALYSIS OF NON-CONDUCTING BODIES BY MEANS OF MELTED SALTS.

By A. DE GRAMONT.

In a previous paper, while describing the dissociation spectrum of silicon in melted salts,[*] I called attention to the fact that the natural silicates, reduced to a fine powder and melted with an alkaline carbonate, give, with the condenser spark, not only the silicon lines, but also the spectra of the bodies which may be combined with them.

A full description of this process and its application to non-conducting minerals, such as silicates, carbonates, oxides, sulphates, &c., will be found in the *Bulletin de la Société Française de Mineralogie*, 1898.

This method gives equally satisfactory results with the insoluble and non-conducting precipitates successively obtained in chemical analysis by the wet way. As in all spectral reactions, the sensitiveness of the test varies with one simple body and another; it is generally better than the blowpipe or wet methods. I therefore thought it would be useful to now give a *résumé* of the parts of this process which can be utilised concurrently with ordinary analysis for examining and checking the precipitates.

A very small quantity of the powdered material suffices, and it does not even need to be dried. It should be intimately mixed in an agate mortar with the salt in which it is intended to be dissolved. A small portion of this mixture is melted in the flame on the flattened end of a thick platinum wire, forming the lower part of the already-described V-shaped connection across the acute angle of which the spark strikes, the two ends being connected to the two poles of the coil and the Leyden jars.

The melted salt used as the igneous solvent of the precipitate should be either carbonate of lithium or of sodium, on account of the simplicity of their spectra. The easy fusibility and superior dissolving power of the lithium salt at a relatively low temperature, causes me to advise its use in all analyses of silicates by igneous disaggregation. The use of other melted salts has been tried. Boric acid and the borates do not give good results; whether melted or in the state of vapour, they form an insulating layer through which the spark strikes with difficulty, giving only the spectrum of platinum (from the wires) and that of the air. Further, the lines of the boron spectrum can only be obtained under quite special conditions, above all with regard to the strength of the spark used. There is therefore no need to use a boron salt as a solvent for other bodies, nor to try and detect boron itself by its dissociation spectrum; it is, on the contrary, necessary to have recourse to the well-known green bands given in the flame by boric acid. We can, however, make use of the alkaline bisulphates for the detection of metals, but a small condensation only—of not more than one jar, for example—must be used, so as to avoid the introduction of the sulphur lines, which would only uselessly complicate the spectrum.

In a case when the nature of the material submitted to examination would give rise to the fear that metallic compounds might be reduced and attack the platinum, the lower spatula should be replaced by a piece of perfectly pure Siberian graphite, hollowed out into a small cup, to contain the melted mixture, and held in the flame by a pair of forceps with platinum points. The source of heat used may be a simple spirit lamp when using carbonate of lithium; with other salts, we must have recourse to the Bunsen burner or a petroleum lamp.

This method has one considerable advantage, viz., the absence of the air spectrum, which does not become manifest until after the complete volatilisation of the melted salt, or when the flame ceases to envelope this latter.

Below are now given some observations on the examination of different simple bodies by the method I have just described:—

Lithium, when tested for with carbonate of sodium, is exceedingly sensitive. When present in very slight traces only, it can be detected by the red line 670·8 and the orange line 610·4. These lines can also be obtained in the cold by allowing the condenser spark to play on a substance containing lithium.

Sodium shows itself by the double Na δ line and the double green Na β, which will indicate the presence of quantities varying from 0·01 to 0·001; the classic double line Na α (D) being always present, either in the melted salt or in the substance under examination.

Potassium, which is not very sensitive to this method, is recognised by its green group K α 583—578, but its violet line 404·6 gives a better reaction.

Rubidium, in traces only, is easily recognised by its two violet lines 421·6 and 420·2.

Cæsium is equally sensitive by its blue lines 459·3 and 455·6.

The alkaline-earthy metals are particularly easy to detect by this method, even in very small quantities. The dissociation of their compounds is easy; further, their arc spectra, studied by Kayser and Runge, are spectra of dissociation, giving the same lines as the condenser spark, as I have verified. It is only the relative intensity of some of the lines that vary within certain limits. We have only to refer to either the original paper by Kayser and Runge ("Ueber die Spectren der Elemente," Berlin, 1891) or to Appendix D of the "Index of Spectra" by Watts (Manchester, 1893) when considering as hardly visible or negligible any lines with an intensity of less than 6 (10 being the maximum). The principal lines, the last to disappear, in their spectra are:—For *calcium*, 445·5, 443·5, and 442·6 in the blue, and especially 422·7 and 396·9 in the violet, and 393·4 in the ultra-violet (these last three lines coincide, as we know, with *g*, H, and K of the solar spectrum); for *strontium*, 460·8 in the blue, 430·6 in the indigo, and 421·6 in the violet; for *barium*, 649·7 and 614·2 in the red and orange, 577·8, 553·6, and 493·4 in the green, and 455·4 in the blue.

Magnesium is characterised by the very sensitive and well known green triplet Mg α 518·4, 517·3, and 516·8; and *glucinum* by the easily seen but decidedly less delicate blue line 457·3.

Manganese is easily recognised by its group of five blue

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[*] *Bull. Soc. Chim.*, 1898, Series 3, vol xix., p. 549. We also find (p. 547, "Spectrum of Carbon") the carbon lines to be deducted from the spectra of the carbonates; in most cases they are reduced to two (657·8 in the red, and 426·7 in the indigo). The lithium and sodium lines in the melted salts are given (*Bull. Soc. Chim.*, 1897, vol. xvii., p. 777).

lines Mn α 482—475. Similarly, *chromium* is characterised by its triple green line 520·9, 520·6, and 520·5; the two latter being difficult to separate with only a moderate dispersion.

Iron and *nickel*, on the contrary, should not be tested for by this method, for even if their lines are not detected, it is by no means safe to conclude that they are not present in the body under examination.

Aluminium, the search for which by means of spectrum analysis is not generally advised, has, on the other hand, given me a very good reaction by its double red line 624·5 and 623·5, slightly diffuse, and almost to be mistaken for a single band. A small quantity of aluminium will show it with great distinctness in the presence of carbonate of lithium, or preferably in this case of a salt of sodium.

Vanadium easily gives its spectrum and shows its presence more especially by a group of strong lines in the indigo, of which the least refrangible 440·8 is the most persistent and the most sensitive; this group extends to 438·0.

Zirconium is easily recognised by its group of five bluish lines, 481·6 to 469; among which 474·0 is the strongest and the last to disappear.

I will not now speak of the line spectra of the metalloids, which have already been described in my researches on dissociation spectra. I will only mention that their sensitiveness, which is very marked in compounds in which they are not combined with oxygen—such as sulphides, selenides, tellurides, chlorides, iodides, and bromides—becomes, on the contrary, comparatively faint in the corresponding oxy-salts, whose dissociation requires a strong condensation (4 to 6 jars) before the lines of the metalloids appear. In such a case, the use of carbonate of soda appears to me to give better results than carbonate of lithium.

The arrangement of the apparatus and the manner of making observations are the same that I have all along used in the examination of melted salts. The spectra obtained are the elementary spectra of the same species, and the greater number of the simpler bodies give satisfactory results by this method.—*Bull. Soc. Chim.*, Series 3, vol. xix.-xx., Nos. 16-17, 1898.

ON THE

VOLUMETRIC ESTIMATION OF COMBINED SULPHURIC ACID.

By MM. F. MARBOUTIN and M. MOLINIÉ.

We have already pointed out a method for this estimation (*Bull. Soc. Chim.*, Series 3, 1897, vol. xvii., p. 953), based on the precipitation of the sulphuric acid in the state of sulphate of barium, the barium remaining in solution being itself precipitated by an excess of chromate of potassium of which the unused portion was titrated by arsenious acid and iodine, the difference in the results obtained, when operating on a sample for analysis and on distilled water, giving the proportion of SO_3 present.

The use of standard solutions does away with many causes of error, simplifies the preparation of the solutions of which one only (iodine) is titrated, and makes it possible to work in a satisfactory manner with materials of doubtful purity.

Several writers (H. Pellet, *Bull. Soc. Chim.*, 1876, vol. ii., p. 251; F. Mohr and Classen, "Traité d'Analyse par Liqueurs Titrées"; Windisch, *Moniteur Scientifique*, 1895, p. 301), and more recently M. Telle (*Journ. de Pharm. et de Chim.*, Feb., 1898), and M. Robin (*Ibid.*, March, 1898), advise the use of equivalent solutions of potassic chromate and chloride of barium. This method, though very enticing at first sight, since the chromium remaining should be mathematically equivalent to the sulphuric acid precipitated, does not appear to us to have that degree of accuracy that the chemist of to-day expects from his analyses.

Without laying too much stress on the uncertainty of the atomic weights of barium and of chromium, the solubility alone of the chromate of barium may easily be the cause of errors, often very considerable.

By taking 137·2 as the atomic weight of barium, and 52·4 as that of chromium, we have observed that in precipitating equal volumes of *so-called* equivalent solutions, in the neutral state, the clear decanted liquid *always contained both barium and chromium.* The amount of chromium was found to be equivalent to 1·5 m.grms. of sulphuric anhydride in 50 c.c. of decinormal solution: this figure, which may appear to be insignificant, becomes of great importance if we compare it with the quantity of sulphuric anhydride contained in the sample taken (10 to 15 m.grms. at the most). We may thus make an error of 10 per cent excess in an estimation by direct reading. The use of a standard solution enables us to make a correction for this error, the amount of chromate of barium going into solution not influencing the results given by the difference between the two readings in any way.—*Bull. Soc. Chim.*, Series 3, vol. xix.-xx., No. 15.

Supplementary Note.—The method for the volumetric estimation of combined sulphuric acid which we have just described is applicable to waters containing only a small quantity of organic matter (springs, rivers, wells). This method can, however, be easily extended to sewages, waste waters, cesspools, &c., after a preliminary treatment for the purpose of eliminating the organic matter such waters contain.

This destruction is effected preferably by fuming nitric acid charged with nitrous vapours. Our method of operating consists in slowly evaporating 200 c.c. of the water under examination with 20 drops of nitric acid on a sand-bath. The cold residue treated with fuming nitric acid is evaporated to dryness. The excess of acid is driven off in the presence of hydrochloric acid; we take up with water, and the clear liquid is submitted to the process already described (*Bull. Soc. Chim.*, Series 3, 1897, vol. xvii., p. 953).

We have thus obtained the results given in Table I.

The variation between the results obtained are only what may be classed as errors of experiment, the limit being 1 m.grm. per litre.

We tried the beautiful reactions given by MM. Villiers (*Comptes Rendus*, 1897, vol. cxxiv., p. 1457) and Lindet (*Ibid.*, 1897, vol. cxxv., p. 246) for the destruction of the organic matters,—that is to say, the use of nitric acid in the presence of a salt of manganese or of vanadium. The estimations made were very satisfactory. The

Table I.

	Estimation by weight.				Estimation by volume.					
Origin.	Organic matter.*	Sample taken.	Weight of $BaSO_4$.	SO_3 per litre.	Sample taken.	Standard.	Reading.	Difference.	Values of I in SO_3.	SO_3 per litre.
	M.grms.	C.c.	M.grms.	M.grms.	C.c.	C.c.	C.c.	C.c.	M.grms.	M.grms.
Biévre	39·0	200	193·3	331·6	50	24·85	14·20	10·65	1·5537	331·0
Collector at Asnières	39·4	200	51·8	88·9	50	22·65	19·85	2·80	1·6012	89·7

* The organic matter is expressed by the weight of oxygen (in m.grms.) furnished by alkaline permanganate of potash, to oxidise 1 litre of water.

destruction of the organic matters is in this case *much more rapid* than with nitric acid only; the solutions thus prepared are very convenient for the estimation by weight.

Table II.

Origin.	SO_3 per litre after treatment with nitric acid. Alone.	With chloride of vanadium.	With chloride of manganese.
	M.grms.	M.grms.	M.grms.
Bièvre	331·6	329 6	332·0
Collector at Asnières	88·9	89·7	89·4

But though the vanadium and manganese remaining do not cause any error in the gravimetric estimation, such is not the case with the volumetric estimation, for which we prefer the use of nitric acid only.

Many writers advise letting the liquid from which we have just precipitated the sulphuric acid by chloride of barium stand for a time in a warm place. We have examined the practical influence of the duration of this digestion on the estimation.

Table III.

Samples.	Weight of sulphate of barium precipitated after— 10 mins.	1 hour.	2 hours.	12 hours.	Differences. Maxima.
	M.grms.	M.grms.	M.grms.	M.grms.	M.grm.
No. 1	297·8	297·5	297·3	297·9	0·6
„ 2	118·6	118·6	—	118·8	0·2
„ 3	58·4	—	—	58·1	0·3
„ 4	30·4	—	—	30·8	0·4
„ 5	13·0	—	—	13·4	0·4
Well water ..	216·0	—	—	216·5	0·5
Water from collector ..	52·2	—	—	52·0	0·2

The differences obtained can only be classed as errors of experiment; they do not exceed 0·6 m.grm. of sulphate of barium, or 0·17 m.grm. of sulphuric anhydride, in the sample taken.

But though the duration of the digestion does not appear to influence the results, this duration has an important action on the manner in which the precipitate is agglomerated. Such a cooling, as slow as possible, of a boiling liquid in which the sulphuric acid is precipitated is one of the essential conditions of an easy and quick filtration: we have therefore adopted the plan of digesting for twelve hours at about 40° for gravimetric estimations. For volumetric estimations the final precipitation of the excess of barium by chromate of potassium clears the liquid to a certain extent, the clear portion only being used, so that we have been able to dispense with this long digestion, and thus greatly shorten the time of the operation.—*Bull. Soc. Chim*, Series 3, vol. xix.-xx., No, 15.

The Composition of Phosphorescent Sulphide of Strontium.—J. R. Mourelo.—The author obtains the most phosphorescent compound by treating a large quantity of strontium carbonate with some sodium carbonate and sodium chloride at a red heat. The mass obtained is then mixed with sulphur and bismuth subnitrate, and heated for four hours at a bright red heat. The product gives an intense phosphorescence. Analysis shows that it contains—besides strontium sulphide—sodium and bismuth sulphide, sodium chloride, and traces of bismuth oxide, and sodium sulphate, in addition to varying quantities of strontium sulphate. Experiment shows that the bismuth is really the active agent when in the form of subnitrate, but its activity is only developed in the presence of compounds of the alkalis. The best results were obtained by using 2 grms. of sub-nitrate of bismuth, 100 grms. of strontium carbonate, 2 grms. of sodium carbonate, and 0·12 of sodium chloride.—*Comptes Rendus*, cxxvii., No. 8.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

THE BANQUET TO PAST PRESIDENTS.

Professor Dewar, F.R.S., President, in the Chair.

(Continued from p. 276).

Professor Odling—"I do not know that I can better commence the few observations I propose to make to you than by following in the wake of my predecessor, Sir Edward Frankland, and saying that it is no less a great pleasure than my bounden duty to express to you, Mr. President, and to the Council and Fellows of the Society, my heartfelt thanks for the great compliment that you have paid to my colleagues and myself on this long-to-be-remembered occasion. Speaking, however, for myself personally, it is not the first time that I have had evidenced to me the kindly feeling of the Chemical Society. On the occasion of my retirement from the Secretaryship in 1869, I had also the special honour done me of being entertained at a dinner by the Society; and I also received a further token of their good will in the form of a capacious loving cup of no inconsiderable value in itself, but of far greater value as a perpetual mark of the kind feeling towards me of those with whom I had been for so many years so intimately connected. Those of us whom you entertain this evening have for a long period of time, as Sir Henry Gilbert and Sir Edward Frankland have already remarked, been associated with one another in common pursuits and enjoyments; and if there is one thing more than another that enhances to me the gratification of this meeting, it is the pleasure of finding myself associated still with my old friends and colleagues, Gilbert and Frankland and Williamson and Gladstone, and my earliest friend of all, Sir Frederick Abel. We have been concerned with one another in a large number of undertakings, and for a long period of time have been accustomed to hear one another's voices as well upon festive as upon scientific occasions. But we have not been accustomed to hear them in exactly the order they have been arranged for this evening. I have always looked upon myself, not as a precursor, but as a follower of Wiliamson. It has been my pride to reckon myself one of his adopted pupils—a disciple of his ideas more perhaps than many of those who were his actual pupils. He was always very decided in his notions. Sometimes, indeed, I turned a little restive, but was always soon pulled up into form again—sometimes more abruptly, perhaps, than was quite agreeable at the moment. At one time I laboured under the sad suspicion of being a little unsound as to the Atomic Theory. Well, perhaps I was not altogether so stalwart in its defence as I ought to have been; but I can assure you that I was never really guilty of so reprehensible a heresy as that which was attributed to me.

"You are doing us honour here this evening not so much, or not only, as students of the science of chemistry, but also as Past-Presidents of the Chemical Society. As ancients of that Society, we may all of us perhaps be permitted to talk a little about ourselves without incurring the imputation of egoism, and also to talk a little about old times without incurring the reproach, after our fifty years' fellowship, of senile garrulity. At the period during which I acted as one of the Secretaries of the Society, and my colleague, Professor Redwood, concerned himself mostly with the business department of our affairs, the Chemical Society had not developed very far its function as a publishing agency, and as a consequence—even for that little prolific time—we did not get our fair share of important papers communicated at first hand to our meetings. But if we did not receive elaborate communications, we enjoyed the benefit of elaborate discussions; and there was no new class of compounds, no newly propounded doctrine, no new reaction which was not submitted to our keen examination and controversy. The subjects of several of those controversies, and even the fashion of them, still linger in one's memory. I need scarcely say that chemical theory came in for a large share of our attention. The molecular weights of water and carbonic acid, the atomic weights of oxygen and carbon, and, above all, the then newly introduced idea of polyatomic radicles, were keenly discussed. We were a little too late for the interesting question as to whether compound radicles could possibly be oxygenous; but still radicles were predominant at that time in chemical science, and reigned with undisputed sway over the whole domain of organic chemistry. One cannot but reflect how fleeting has been their reign. The doctrine of radicles has now sunk to an entirely subordinate position in chemistry, not unlike, may I venture to say, the subordinate position into which radical doctrines have fallen in a different sphere. There was one particular controversy I remember very well, and am sure Frankland will remember also. It was of this kind: whether the bodies called ethyl and methyl were really ethyl and methyl at all, or something else. Well, a question of that kind in those unsophisticated days had to be answered definitely by a plain aye or no. There was no loophole for escape or trimming, no possibility of saying that the one answer was just as true as the other, according to the point of view taken; nor was there existent in that period of innocence, for the solution of yet more puzzling problems, what we know now by the name of tautomerism, by which we learn that a body is, and at the same time is not, what it is alleged to be; that it is sometimes one thing and sometimes another, and sometimes both together, and yet preserves its individual chemical entity. In those days the principal provider of chemical material for our meetings was far and away Hofmann. He was in the habit of sending his multitudinous papers to the Royal Society for publication; but he gave us the advantage of his presence and his personal disquisitions; and I would appeal to all in this room who had the advantage of seeing him, to say if they can possibly forget his appearances at the blackboard of the Chemical Society, and the enthusiasm and lucidity of his expositions of different points of chemical constitution, enlivened as they were by that extraordinary display of vivacity so inconsistent with the quiet phlegm we are in the habit of attributing to those of his nationality. But, despite the productiveness of Hofmann, still there were evenings on which something else was required; and then it behoved the Secretary to search far and wide for material to bring before the meeting of chemists who, with Greek-like avidity, were always clamorous for 'some new thing.' At that period the activity of the Giessen school was somewhat on the decline, and we loooked for novelties in chemistry, as for novelies in mantles and millinery, to Paris. We had for our consideration the acidic ammonias of Gerhardt and the diatomic glycols of Wurtz, and the production of alcohol without the aid of either sugar or yeast by Berthelot, and many other remarkable contributions to the knowledge of the day. But our friends across the water, with so much—so very much—justly due to them, nevertheless did manifest now and then a tendency to appropriate to themselves what did not altogether belong to them; and in this, the country of Black and Priestley and Cavendish and Dalton and Davy, we were astonished one fine morning at being informed that 'la Chimie est une science française.' But even with the productiveness of Hofmann and the searchings of the Secretary, it did sometimes happen that our bill of fare was a little meagre. But what of that? Those were supper-eating days, and a meeting rendered brief by want of pabulum could always be supplemented by a prolonged and substantial, and, I may add, a musical, meal at a then well-known resort not far from Covent Garden; and when it happened, as it did sometimes, that our proceedings were not so exhilarating as they should have been, when divine philosophy had proved less charming than its wont, Hofmann, despite the abundant supply of tea and coffee of excellent quality, would, with a burst of inspiration, thrust forth his right hand, and say 'I will tell you, we will have a punch!'

"But the Chemical Society has a future to look forward to, as well as a past to look back upon. At the Jubilee of the Society some seven or eight years ago, it devolved upon me to give an account within the short period of a quarter of an hour—I believe I occupied twenty minutes—of the progress of chemical science during the preceding fifty years. But to-day is also a Jubilee, or almost so, the Jubilee of our incorporation by Royal Charter, which, in the then days of our insignificance, Playfair did so much to obtain for us. Now, on this diamond Jubilee, I ask you how many minutes will you give me to lay before you a forecast of the chemical progress that may be expected to take place within the next fifty years? I will only venture to say that, judging by the number and activity and intellectual gifts of the workers of the present day, we may feel assured that the achievements of English chemistry and the progress of the Chemical Society in the past, will be as a mere nothing to the brilliancy to which they will attain in the future."

Sir Frederick Abel—"Sir Edward Frankland has out of his vast stores of knowledge recalled a fact of which I confess I was ignorant, that in years past I indulged a poetic fancy. I only wish I might now be inspired in order to find words to express on behalf of myself and my old friends our appreciation of this glorious reception which you have given us. The Chemical Society is endeared to me in many ways. Among the epochs of a somewhat long career of ceaseless activity, that which connected me intimately with the work of the Society is one of those which I recall with the greatest pleasure and satisfaction. And it so happens that the years of my connection with the Society in various functions were years in which some of the most memorable events in its annals occurred. As Treasurer, it was my privilege to arrange with the illustrious chemist and brilliant orator, Jean Baptiste Dumas, for the delivery of the first of those memorable lectures which were given through the agency of the Chemical Society in honour of the memory of Michael Faraday. While I was Treasurer, the volume of the Journal of the Society, which was then of modest and slender dimensions, nurtured by well-digested extracts from foreign journals, speedily gained proportions unwieldy in character, so unwieldy, in fact, that the one volume split up into two before long. In the first year of my Presidency, the Research Fund, which was initiated in a modest manner by Mr. Thomas Hyde Hills, was placed upon a firm and substantial basis through the generosity of one of the most respected of the Society's original members, Dr. Longstaff; and in the second year in which I held that office, the somewhat revolutionary agitation which was persisted in by a not unimportant section of the younger Fellows of the Society,—an agitation which, by the way, has been imitated since,—led to earnest deliberation and consultation between the Council and some of its chosen members outside the Council, which resulted in the birth of an institution now flourishing exceedingly, which has become the guardian of the best interests not only of the chemical profession but also of the public. I of course allude to the Institute of Chemistry of Great Britain and Ireland. When I look back to the early days when I first owned the proud title of F.C.S., and remember my attendance, in a small room at the Society of Arts, at the meetings of the Chemical Society, presided over in succession by William Brande and Phillips, the business being managed by George Fownes and Robert Warington, the founder of the Chemical Society, and the funds not very cleverly handled by dear old Robert Porrett, one of the most prominent forms that appears in my mind's eye is that of the favourite pupil of Liebig, my venerated master, Hofmann. In the very first years of the Society, Hofmann became the very life and soul of it. He was beloved by his English brethren directly he came among them, and for years he was by far the most prolific contributor, either himself or through his pupils, to the volumes of the Society. Pardon me if I have been tempted into reminiscences; it is difficult to avoid it at such a gathering as this. The welcome you have given to the veteran Past-Presidents will remain in their minds to their last day as one of the great joys of their lives. To the many old friends and colleagues whom I see around me—Past-Presidents who, as men of science, hold positions second to none, whose names are familiar as household words—to them I can wish no higher gratification than that they may live to experience the satisfaction of such an entertainment, and of such a graceful appreciation of their work, as has been the lot of your old Past-Presidents to-night."

Professor **A. W. Williamson**—"I thank you, Mr. President, most heartily for the kindly words you have uttered in relation to me and to my efforts for the advancement of chemistry. It is an immense satisfaction to me to see a man of your talents and vast acquirements placed in so influential a position as that which you so worthily occupy. But whilst thanking you I am bound to confess that I have been for some time past a most unworthy member of the Chemical Society. It happened that after a good many years of work in our Society, I had other matters of such importance claiming my time and attention, that I was unable to continue to work amongst my colleagues and friends in the Chemical Society.

"Before I came over in 1849 to work at University College, I had become acquainted in the Giessen Laboratory with that most remarkable man August Wilhelm Hofmann, and I may mention a characteristic incident illustrating his earnest and steadfast devotion to his science. He had for a considerable time been working at derivatives of aniline, and in order to carry on these researches as effectively as possible, he prepared by the action of caustic potash on indigo about some two gallons of aniline. The product was placed in a big bottle on the mantelpiece in his bedroom, and the story goes that he used to stand and gaze at it for some time every morning and evening, and gloating over it with delight would think 'What a number of splendid products I shall make out of this aniline!' The energy and devotion with which he followed up his work on the derivatives of aniline, at the expense of many other researches which he might with advantage have followed up, was such that he came to be talked of as the great worker on aniline, and Sir Benjamin Brodie somewhat prematurely wrote his epitaph in the following words: 'Hic jacet Aniline.' His researches extended, however, at an increasing rate into other and wider departments of chemistry, and his energy and enthusiasm were such as to make him the leading explorer in the domain of organic chemistry. Berzelius had been for a lengthened period the one great man in the domain of inorganic chemistry, which was the only part of the science which had been explored to any appreciable extent. When I saw the vast piles of knowledge which Hofmann was so rapidly accumulating in the new domain of chemistry, I felt, and ventured to say, that his masterly labours entitled him to be called the Berzelius of Organic Chemistry. I happened to be present at a meeting of the Chemical Society at which a young chemist read a paper in the presence of Hofmann on some theoretical matters of importance which had already engaged the attention of distinguished chemists. Hofmann did not enter into any particulars of the paper, but he gave vent to an outburst of heartfelt delight at the simple narrative which had been read. There are various incentives to work, but the most potent incentive to earnest and efficient work is probably the example of a man like Hofmann, whose whole delight lay in mastering the truths of science, and in learning more and more particulars of the order of Nature, and Hofmann possesssed that power in a most eminent degree.

"We see in this grand hall an assemblage of chemists known by their earnest labours and valuable discoveries, and we are honoured by the presence of men of the highest distinction in other branches of science, as well as of leaders in the learned professions. It might not be unreasonable to believe that enthusiastic delight in the triumphs of chemical research is duly represented by some of the guests in this hall, and that the lively conversation which has been going on may not relate merely to high questions in jurisprudence, medicine, or legislation, but that some samples of chemical enthusiasm may reach the ears of the learned representatives of other professions.

"I feel sure that at a future time we shall all look back with the highest pleasure upon this delightful evening, which we owe to the kindly exertions of our President and other leading members of the Society.

Dr. **John Hall Gladstone**—"It is a pleasant thing to look on the faces of so many friends with whom one has worked in olden times, with whose works one is well acquainted; though, of course, there are many at the present time who come into the Society, and whom I can look to as budding philosophers: unfortunately, I do not know their names so well as their faces. The pleasure is not merely because we call ourselves chemists, but because there is a bond of union between us arising from the desire of discovering the wonderful secrets of the great cosmos of which we ourselves form part. There is a great difficulty in speaking to you this evening, because so much that I should have liked to say has already been said by previous speakers. Still there are one or two things which, if you will permit me, I should like to bring before you. First of all, in your too flattering description of myself and of my work—which makes me rather ashamed to stand up and speak—there was a point which I think calls for remark, and so I must venture upon that which characterises the speeches of all of us, a certain amount of early autobiography. I was exceedingly fond of science from a little child. My favourite science was geology, and also what could be seen in the microscope—infusoria, and other little objects we have heard of in later times. But, in choosing a profession, my father said geology was not a promising career, and recommended chemistry. I knew very little about it, but went to University College and studied under that admirable teacher Professor Graham, and afterwards under Liebig. I suppose it was from Graham that I acquired the taste for the physical side of chemistry and its connection with heat, light, electricity, and other forces of nature. I looked out for a scientific position, and lectured at St. Thomas's Hospital for some time, made analyses, and considered myself a professional chemist. It may be that circumstances have caused me to sink into the position of an amateur chemist, but my first intention was that of following chemistry as my profession in life. It has not been necessary to continue that; and I have had this advantage, that I could always keep in my laboratory a good trained assistant, and thus, whilst I was engaged in other works and ways, and in endeavouring to extend the knowledge of chemistry and elementary science in our primary schools, the work still went on more or less under my immediate direction. I should have liked to have said something about the progress of chemistry during these past fifty years; but the subject is so enormous, and you yourself have touched upon it to such an extent and so well, that I need only allude to the fact that this great change of volume of chemistry has caused it to be necessary that we should specialise. Specialisation has its advantages, but also its disadvantages. One danger is that we may become narrowed in our views. So it would appear best to have a home somewhere or other, but to make occasional excursions in the neighbourhood, and take summer holidays so as to get our nerves braced up to work again at our own pet subjects. I must not touch upon other points, such as the relations of the physical forces to chemistry, or its useful applications, and the great value of chemical research for the welfare of mankind. These are subjects too large and important to enter upon at this late hour. It seems to me that while we are always increasing the mass of knowledge we possess, the space which we see to be bright becomes larger and larger, but there is beyond a dim nebulosity. It is our work to bring from that nebulosity something into the bright space, so that it becomes the property of the human race. But there is beyond this a region which we do not understand—infinite as far as we know—and our object is to increase that which is knowable, in the firm belief that it will be for the advantage of our fellow creatures. While I feel thankful for the joy that I have had in taking some part in these discoveries, I cannot look to have much more time given me for carrying on this work of investigation; but still there may be a few threads of old research I may gather up, and in doing so I shall be greatly encouraged by the kind remarks of this evening, and the way in which our work has been received by the friends gathered around us."

(To be continued).

NOTICES OF BOOKS.

Report of the Senior Analyst of the Cape of Good Hope for the Year 1897. Cape Town: W. A. Richards and Sons. 1898. Pp. 88.

The number of articles analysed during the past year, though slightly in excess of that of 1896, is still rather less than in 1895. This decrease is attributed to a change which has been effected in the administration of the Adulteration Act. The number of samples examined in 1897 was 979, and consists of every variety of substance; milk and water being the most frequently done. Supposed gold ores show a considerable falling off, the numbers being 44 in 1896 against 27 in 1897; while there are no less than 28 new substances in the list which were not previously dealt with, such as condensed milk, bread, honey, rice, glycerin, quinine wine, henbane, zinc, &c. The money value of the analyses made was £1270 4s. 9d., being an increase of about £150 over that of any previous year.

Of 549 samples of foods examined, 104 were found to be adulterated, the chief offenders being milk (fresh and condensed), coffee, and brandy; but it is satisfactory to note that the proportion of adulterated articles has fallen from 30 per cent in 1894 to only 19 per cent in 1897 of the total number examined.

Forty-four samples of water have been analysed during the year. We are, however, surprised to read that an analysis of water from the Table Mountain reservoirs contained as much as 5·46 grains of organic matter per gallon; surely this must be a misprint, the total solids are only 9·24 grains per gallon.

A large number of analyses have been made of soils and manures, an important subject for an agricultural colony like the Cape of Good Hope, and a number of maps, diagrams, and curves showing the results are to be found at the end of the report. It is, however, proposed to suspend these investigations for awhile in order to devote time to other more important agricultural questions.

Thirty-fourth Annual Report on Alkali, &c., Works. By The Chief Inspector. Proceedings during the Year 1897. London: Eyre and Spottiswoode. 1898. Pp. 129.

Since the publication of the last Report, Sub-Inspector Mr. B. E. Smith has resigned his position, which has been filled by the appointment of Mr. J. W. Young, B.Sc., who will take charge of No. 2 District, comprising the northern counties of England.

The number of works now registered under the Acts in England, Ireland, and Wales is 1058; of these, only 87 are works decomposing salt, and therefore described as alkali works, while the remaining 971 are scheduled under the Acts of 1881 and 1892. These figures show a decrease of 11 alkali works and 5 other works since 1896. There are also 125 works registered in Scotland, bringing the total number up to 1183.

The total number of visits made in England, Ireland, and Wales during the year was 4116, and 4562 tests were made. It must, however, be borne in mind that no figures are given regarding No. 2 District, and that one of the inspectors was incapacitated for ten months owing to a serious accident, otherwise these numbers would have been considerably larger.

It is very satisfactory to see that there have only been three prosecutions under the Act, and that these were not very serious cases.

The number of works using the Leblanc process shows a reduction. Nevertheless, great activity is displayed in those works remaining in operation, requiring close attention from the inspectors.

Reviewing the industry as a whole, the Chief Inspector states that he has every reason to be satisfied with the care displayed and the competence shown by the management, so that in no single case has the question of prosecution for infraction of the Act assumed a serious shape; complaints of damage to crops have almost ceased. The effect of sulphide of calcium in presence of iron salts in sewage as a germicide has received some attention at the St. Helens sewage works.

It has been also noticed that the vapours evolved on the running off of pitch are so highly valued as a remedy for children suffering from whooping cough that, by permission of the owners, many patients were sent to the works to inhale the vapours given off during the progress of the operation. It is also pointed out that, during epidemics of infectious diseases, the cases notified within the chemical work's area were always lower than in other districts; while the general death-rate per 1000 is as 16·6 to 10 in favour of the chemical work's area in 1893, and 14·4 to 9·2 in 1896.

The reports from the different sub-inspectors fill a large portion of the book, close details and tabulated results being given of the work done during the year.

Report of the Chemist at the Central Experimental Farm, Canada. By F. T. Shutt, M.A., F.C.S. 1896. Author's Edition. Ottawa: Government Printing Office. 1897.

The matter here reported on is briefly outlined under the headings of Soils, Mucks and Muds, Manures and Fertilisers, Fodders, Waters, and such like.

We are sorry to see that there was a disastrous fire in the laboratory in July, caused by the accidental bursting of a flask of boiling sulphuric acid. Nearly all the apparatus was destroyed, but the greatest loss was in samples and records—the accumulation of nine years' work.

Some instructive results obtained by fermenting manure for one year in a shed are given. They show that there was a considerable loss of fertilising constituents during that period. Finely-ground mineral phosphate was mixed with strongly fermenting manure, but the results showed that practically no phosphoric acid was thereby made available.

As in past years, the analysis of well waters from farm homesteads has been continued, the results showing plainly that in many cases polluted water is being used, 45 per cent of the samples were very seriously polluted, 20 per cent were suspicious and probably unsafe, while only 35 per cent were returned as wholesome and fit for use.

Lectures on Physical Chemistry. Delivered at the University of Berlin by J. H. van 't Hoff. ("Leçons de Chimie Physique Professées a l'Université de Berlin"). Translated from the German (into French) by M. Corvisy. Paris: A. Hermann.

This volume is devoted chiefly to a consideration of "Chemical Equilibrium"; that is, to the limiting conditions in which chemical bodies can exist in stable equilibrium.

Starting with the simple examples—"Water" (which can, at suitable temperatures and pressures, exist in two or three forms in contact) and "Sulphur" (which can similarly exist in two, three, or four forms)—the Professor goes on to discuss the more complex cases of a salt in solution (where concentration enters as a condition), then of two salts (which may or may not have a common base, and in which double decomposition may or may not take place).

The conditions of stable equilibrium are expressed in simple formulæ, involving a slight acquaintance with the calculus, based upon the laws of Boyle, Gay-Lussac, Avogadro, and others.

These simple reactions have been well worked out by many observers, and it is interesting to note the close numerical agreement between the theoretical and observed results.

The formulæ are also applied to more complex reactions still, and a certain measure of agreement, though not so close as before, found between the theoretical and the scanty experimental results.

Section II. is concerned with the rate at which chemical reactions take place, and with the mechanical and electrical measurement of the force of affinity between different molecules. The various causes which modify the rapidity of a reaction are considered one by one, and the laws governing them set forth. The effects of pressure, temperature, and dilution are clearly marked, but the effect of the wave propagated in an explosive mixture of gases is still undecided; various empirical formulæ have been suggested, but they do not in any case fit more than two or three of a series of experimental results.

The volume is a valuable contribution to the records of modern scientific research.

CORRESPONDENCE.

THE PROPERTIES OF LIQUID MIXTURES.

To the Editor of the Chemical News.

Sir,—In the abstract of my communication to the Physical Society, in connection with Mr. R. A. Lehfeldt's paper on the above subject (Chem. News, lxxviii., p. 276), the most probable explanation of the fact that, when American petroleum is distilled, the benzene comes over at about 65° instead of 80°, is stated to be that "benzene and hexane behave, as regards distillation, *like miscible liquids.*"

This should read "*like partially miscible liquids.*"

The two liquids are, in fact, miscible in all proportions, and the point is that, in certain respects, they behave as though they were only partially miscible.—I am, &c.,

Sydney Young.

University College, Bristol.
December 6, 1898.

THE GASES OF THE ATMOSPHERE.

To the Editor of the Chemical News.

Sir,—If your readers could not expect Professor Ramsay to reply to my last letter, I am sure they were yet further from expecting Professor Tilden to rush in where that angel feared to tread.

Agreement is always delightful, therefore I am happy to agree with Professor Tilden in thinking that chemists have heard enough about the respective shares of Lord Rayleigh and Professor Ramsay in the discovery of argon. Unfortunately, Professor Ramsay is of a different opinion, and is constantly endeavouring to alter the distribution to his own advantage. It would no doubt suit him very well to see these efforts passed *sub silentio.*

In my last letter I showed that Lord Rayleigh and Professor Ramsay have given entirely different accounts of the same simple occurrences. I quoted the two narrations so that everyone could see for himself. Professor Tilden apparently cannot see; and it might aid him were you to print the thing in parallel columns, thus:—

Lord Rayleigh	*Professor Ramsay*
Said, in 1895, that his own researches suggested to him the question whether the so-called nitrogen of the air is all of one quality.	Says, in 1898, that it was he who suggested this question to Lord Rayleigh.
That he propounded this question to Professor Dewar, who referred him to the Cavendish experiment made a century before.	That it was he who directed Lord Rayleigh's attention to the work of Cavendish.
That when the suggestion was made to him, he at once saw its importance, and quickly followed it out, finding that Cavendish had put the same question as himself.	That Lord Rayleigh did not at first attach much importance to the suggestion, and thought it more likely that different compounds contained different kinds of nitrogen.
Wrote a letter to *Nature* on September 25, which was published on September 29, 1892.	Says that this letter appeared early in 1894, and that it was the immediate cause of his entering into the field at that date.

Here we have three categorical statements made in public by Professor Ramsay which are irreconcilably opposed to Lord Rayleigh's lucid and straightforward narration, and a fourth statement which a reference to *Nature* shows to be incorrect. Two of these statements are in disparagement of Lord Rayleigh, one in disparagement of Professor Dewar, and all four are intended to glorify Professor Ramsay at their expense. This is the case which Professor Tilden ought to have been prepared to deal with when he entered the arena. The issues, be it observed, are simple questions of historical accuracy depending upon ascertainable facts and the relative credibility of different witnesses.

Professor Tilden has not dealt with the case at all. His nearest approach to dealing with it is a sorry quibble relating to one point out of the four. He asks how I am to know what conversations Lord Rayleigh had with chemists, or how many of them mentioned the Cavendish experiment to him. I do not know, nor do I care in the least; a dozen men may have referred to Cavendish in conversation, but only one man can have "directed his attention" to the Cavendish experiment or told him anything about it which he did not already know. Lord Rayleigh says that Professor Dewar was the man who did him this service. Professor Ramsay says that he was the man. I believe Lord Rayleigh: first, because he has never been known to say the thing that was not; and second, because he is the only man living who can speak with absolute certainty upon the point. Professor Tilden prefers to believe Professor Ramsay. That only proves what is abundantly evident from the rest of his letter—that Professor Tilden does not cultivate the scientific habit of mind.

For the rest of his letter is wholly irrelevant. It is composed of an imputation of malice, a sniff at anonymity, a superfluous certificate of character and reputation to Lord Rayleigh, an absurd attempt to infer his private sentiments from his remarks upon an occasion when their obtrusion would have been an offence against good taste, and—worst of all—a most lamentable exhibition of incapacity to understand how a gentleman would act if in an official capacity he had to deal with the case of a man with whom he had a private difference. Quite as a matter of course, Professor Tilden bases an argument upon the tacit assumption that if Lord Rayleigh had felt privately aggrieved by Professor Ramsay, he would have used his influence as an official of the Royal Society to prevent the bestowal of the Davy Medal. In the case supposed, I am convinced that Lord Rayleigh's conduct would have been of a diametrically opposite character. From this argument I infer that Professor Tilden is even less than myself in the confidence of Lord Rayleigh.

For the sake of clearness—it seems impossible to be clear enough for some people—I will repeat that the first and third points upon which Professor Ramsay flatly contradicts Lord Rayleigh are not met by his apologist in any way. One contradiction represents Lord Rayleigh as incompetent to draw an obvious inference from his own work without the assistance of Professor Ramsay. The other represents him as too dull to see the value of a suggestion coming from the same "universal provider," who we must infer kindly carried on Lord Rayleigh's education until the importance of the Cavendish experiment at length dawned upon him. On the fourth point, the mistake as to the date of Lord Rayleigh's letter to *Nature*, Professor Tilden has not a word to say. Most significant of all, he shirks entirely the damaging conclusions which I drew from the whole case, and the challenge for the production of evidence in support of assertions. When the eminent authority upon science and morals, or his apologists, shall have fairly faced and disposed of the awkward facts of the case, instead of dealing in ridiculously inept inferences concerning Lord Rayleigh's private sentiments, I fancy they will have little stomach left for inquiring into the motives or the personality of—Yours, &c.,

SUUM CUIQUE.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvii., No. 8, August 22, 1898.

Oxides of Sodium.—M. de Forcrand.—The author studies the products of the direct combustion of sodium in dry air free from carbon dioxide. The experiments take place in a small retort attached to a large globe, through which passes a slow current of air. Slightly below its fusing-point, the sodium becomes covered with a grey layer, which soon increases in volume if the experiment is stopped at this point. If, however, the heating is continued, the grey substance ignites in the current of air, and the vivid combustion is accompanied by two phenomena:—(1) White vapours are produced, which are very volatile and condense only in small quantities in the retort and globe. (2) As the grey substance burns, it is transformed into a yellowish substance, which becomes nearly white on cooling. These products are examined and analysed. The grey substance formed at first has the composition Na_3O; the white volatile powder, Na_2O_2; and the white substance, which is yellowish when hot, is a mixture or Na_2O_2 and Na_2O. Na_2O_3 is not formed by this method.

Ammoniacal Chlorides of Lithium.—J. Bonnefoi.—The author investigates the four possible combinations of lithium chloride and ammonia. $LiCl.NH_3$ is formed when LiCl absorbs quite pure and dry NH_3 at temperatures above 85° and atmospheric pressure; the compound formed being kept above 85°. $LiCl.2NH_3$ is formed under the same conditions between 60° and 85°. $LiCl.3NH_3$, between 20° and 60°; and $LiCl.4NH_3$, the saturated compound, below 13°. Measurements show that the heat of combination diminishes in proportion as the new molecules are added; while, at the same time, the stability of the compound diminishes, and the dissociation tension becomes greater for the same temperature. The numbers for the heat formation, calculated by Clapeyron's formula, agree in all cases with the direct thermo-chemical measurements.

No. 9, August 29, 1898.

This issue contains no chemical matter.

No. 10, September 5, 1898.

Silicide of Tungsten.—E. Vigouroux.—Moissan has determined that silicon and tungsten combine if heated together in the electric furnace. The author investigates the properties of the substance formed. He heats together silicon and tungsten oxide, obtaining a heavy whitish mass. To obtain from this the tungsten silicide, the mass is suspended in a dilute solution of HCl as the positive pole, the negative pole consisting of a rod of carbon connected with a battery of two or three cells. The combined action of the acid and current dissolves away the metal, the silicide remaining intact. The crystals of silicide fall to the bottom of the vessel as they are liberated. These are treated first with aqua regia and then with ammonia, to remove the last traces of tungsten, and pure Si_3W_2 is left, which is crystalline, in the form of metallic-looking plates. It is heavy, having a density of 10·9; it is attacked by chlorine, bromine, and iodine at temperatures of about 300—500°; it burns brilliantly in pure oxygen at about 500°. Hydrochloric and nitric acids have no action in the cold; also the action of aqua regia is inappreciable; but a mixture of nitric and hydrofluoric attacks it violently. Silicide of tungsten is analysed in the following manner:—The silicide, contained in a glass vessel, is decomposed by chlorine at a high temperature; chlorides of tungsten and silicon are formed. The silicon chloride, being more volatile, is separated, converted into silica, and weighed. The metallic chloride is treated with nitric acid, forming tungstic acid, which is calcined and weighed.

The Solubility in Water of Tricalcic Phosphate and of Apatite.—Jules Joffre.—The solubility of tricalcic phosphate in water is a question of great interest to chemists and others engaged in agriculture; for, however slight this solubility may be, it is of great importance in vegetable physiology. The author placed the phosphate in water for about two months, then filtered, and, after evaporation, the phosphoric acid was estimated as phospho-molybdate of ammonia. There is good reason to believe that two months is a long enough time for contact with water; for, after a submergence of several years, the author found analogous figures. The coefficient of solubility is found to be 0·009 grm. per litre. As carbonic acid is always present in the soil, the author made further experiments with water saturated with carbonic acid at the normal temperature, and found that the coefficient of solubility was 0·153 grm. per litre. He next made similar experiments with apatite, both in pure water and in water charged with carbonic acid. In pure water there was only 0·002 grm. per litre dissolved, and in water saturated with carbonic acid 0·014 grm. per litre.—*Bulletin de la Société Chimique de Paris*, Series 3, vol. xix.-xx., No. 9.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 5th inst., Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, presiding. The following were elected Members:—Herbert William Allingham, F.R.C.S.; Mr. T. Newbold Piddocke: Mr. Edwd. Preedy; Mr. William Munro Tapp, LL.D.; The Hon. William Frederick Cuthbert Vernon; Mrs. Adela Wetzlar, and Dr. Charles Theodore Williams, F.R.C.P. The special thanks of the Members were returned to Dr. George Wyld, for his present of a portrait of Dr. Thomas Garnett, first Professor in the Royal Institution.

City and Guilds of London Institute.—The following Scholarships have been awarded in connection with the present Session, 1898-99, of this College:—Clothworkers' Scholarship, £60 a year, to A. J. Cook; Mitchell Scholarship, £50 a year, to R. H. Collins; John Samuel Scholarship, £30 and free education, to F. C. Hounsfield; Institute's Free-Studentships, to R. H. Buckie, A. W. Harrold, and W. H. P. Brounger.

A Catalogue of Scientific Books and Periodicals.—We have received the first number of a new publication entitled *Bibliographie des Sciences et de l'Industrie*, which will be published on the 5th of each month, and sent free of cost to anyone who applies for it. The object of the publication is to give in a concise form a summary of all the new books and periodicals bearing on scientific subjects, viz., electricity, chemistry, architecture, geology, mathematics, and legislation, both administrative, industrial, and commercial. The prices of all these publications are given, and any of them will be sent on receipt of a postal order or cheque. This catalogue is issued by Vve. Ch. Dunod, 49, Quai des Grands-Augustins, Paris.

Estimation of Tannin.—Léo Vignon.—A new method of estimating tannin is based on the following principle:—Given an aqueous solution of tannin, this substance, to the exclusion of other bodies which generally accompany it (gallic acid, glucose, &c.), is absorbed readily and almost in entirety by undressed silk; it is sufficient to keep the silk-tannin mixture dissolved from four to five hours at 50° C. and to use the silk in large excess of the tannin. The tannin thus absorbed may be estimated by several methods, of which the most exact is described at length.—*Comptes Rendus*, cxxvii., No. 8.

NOTES AND QUERIES.

⁎⁎ Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Queries.—(1) What are the estimated specific gravities of liquid oxygen and of liquid hydrogen. (2) What is the crystalline form of the element manganese, and where would one find a thorough treatment of the physical properties of the element manganese?—W. L. T. Addison, Byng Inlet, Ontario, Canada, Nov. 16, 1898.

MEETINGS FOR THE WEEK.

Monday, 12th.—Society of Arts, 8, (Cantor Lectures). "Acetylene," by Prof. Vivian B. Lewes.

Wednesday, 14th.—Society of Arts, 8. "Commercial Education," by Sir Albert Rollit, M.P.

Thursday, 15th.—Chemical, 8. "Interaction of Ethylic Sodiomalonate and Mesityl Oxide," by A. W. Crossley, Ph.D. "Derivatives of Camphoric Acid," Part III., by F. S. Kipping, D.Sc., F.R.S. "Synthesis of $\alpha\beta\beta$-Trimethylglutaric Acid," by W. H. Perkin, jun., F.R.S., and J. F. Thorpe, Ph.D.

THE CHEMICAL NEWS.

VOL. LXXVIII., No. 2038.

PREDICTIONS OF NEON.

By Lieut.-Colonel W. SEDGWICK, late R.E.

IN Lord Lister's Address at the Anniversary Meeting of the Royal Society on November 30th, 1898, reference was made to the fact that there were grounds for anticipating the existence of a non-valent element of the atomic weight of neon.

In the CHEMICAL NEWS, vol. lxxi., pp. 139—140, I showed that the metalloid series—

$\mathrm{Fl}^{\mathrm{I.}}$, 19; $\mathrm{O}^{\mathrm{II.}}$, 16; $\mathrm{N}^{\mathrm{III.}}$, 14; $\mathrm{C}^{\mathrm{IV.}}$, 12

pointed strongly to the existence of a non-valent element of atomic weight 20; and that one of the metal series also pointed just as strongly to the same fact; and thus that both of these series had been derived from a non-valent element of atomic weight 20. The metal series in question was, of course—

$\mathrm{Na}^{\mathrm{I.}}$, 23; $\mathrm{Mg}^{\mathrm{II.}}$, 24; $\mathrm{Al}^{\mathrm{III.}}$, 27.

But I further showed that, in "Force as an Entity," published in 1890, I had (at p. 61) previously pointed out in effect that the above metalloid series showed the probable existence of a non-valent element of atomic weight 20; and (in a paper submitted to the officers of the Royal Society on November 16th, 1892) that the metalloid and metal series both showed the same fact. I may add that in that paper, which was on "The Form of the Atom," I showed a non-valent element of atomic weight 20—21 as "assumed to exist," bringing forward both the metal and the metalloid series shown above to support the assumption, and pointing out the probability that both of these series had a common origin in a non-valent element of that atomic weight.

On each of these occasions my object in pointing out the probable existence of this and several other non-valent elements was to show that with these non-valent elements it was possible to deduce the form of the atom, both for metals and metalloids; the form obtained being, for non-valent atoms a perfect sphere, and for valent atoms a sphere with flat places in number corresponding with valency—the monovalent having one, the divalent two, and so on. In the metalloid atom the flat places are cut down, so that atomic weight decreases as valency increases; and in the metal atom they are built up, so that atomic weight increases as valency increases; and, accordingly, the same non-valent element can give rise both to a metalloid and a metal series.

Professor Julius Thomsen in *Zeit. für Anorg. Chemie*, vol. ix., p. 283, refers to my paper in the CHEMICAL NEWS, vol. lxxi., p. 139, in giving his conclusions in regard to the origin of the elements based on their electrical behaviour. He obtains a diagram which manifestly finds a perfect and complete physical expression in the form for the atom obtained from valency as shown above.

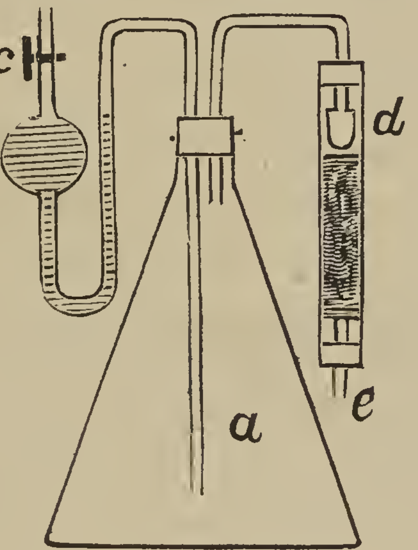
In regard to Clerk-Maxwell's objection that the hard atom "fails to account for the vibrations of the molecule as shown in the spectroscope" (Art. "Atom," "Ency. Brit.," 9th ed.), it may be pointed out that, with an ether composed of two fluids, it is not necessary to refer the disturbance which gives rise to light to any vibratory movement in the atom. Our ocean waves and ocean breakers are not due to any vibratory movement in our earth, but are due to the presence of two fluids. And we may remember that Newton said in effect that he would accept the undulatory theory of light if he could see his way to getting an ether composed of two fluids ("Opticks," 3rd ed., p. 339).

December 12, 1898.

A SIMPLE APPARATUS FOR THE ESTIMATION OF CARBON DIOXIDE.

By W. H. BARKER, B.Sc., F.C.S.

THE construction of this apparatus can easily be understood from the figure. It consists of a conical-shaped flat-bottomed flask, fitted with a cork having two holes. Through one of these holes is inserted a bent glass tube, the drawn-out end of which nearly touches the bottom of the flask; near the other extremity of it a bulb, *b*, is blown, in which the acid is placed. The tube may be opened or closed by means of a short piece of rubber tubing provided with the clip *c*. Through the other hole of the cork is inserted a bent glass tube connected with a straight $CaCl_2$ tube, in the upper part of which is placed the closed end of a test-tube, *d*, about an inch long, the rest of the tube being filled with $CaCl_2$. This arrangement prevents the $CaCl_2$ from becoming unnecessarily moist.



In carrying out an analysis, after the carbonate has been placed in the flask and the necessary weighings made, a rubber tube is attached to *e* and the clip *c* opened. By suction through the rubber tube a small quantity of acid is drawn into the flask and the clip is quickly closed. The bent tube with the bulb containing the acid now acts as a syphon, and therefore, by means of the clip, the flow of acid into the flask can be regulated. The analysis is completed by warming the flask and aspirating air through the apparatus by suction through the rubber tube, which is removed before the final weighing is made.

NOTE ON THE

DESTRUCTION OF SOAP BY WATER.

THE SOAP TEST AND LIME WATER.

By ROBERT MELDRUM, F.C.S.

THE following experiment as regards the destruction of soap by hard water, though not so accurate as it ought to have been, is nevertheless interesting, as the number of such determinations pubished is not very numerous.

The water experimented with had a total hardness of 38° per gallon,—permanent 22°, temporary 16°,—and was fairly constant. A pint of the water was taken, to which was added 1 grm. of the soap (primrose) dissolved in a little of the water and well shaken. The lather produced disappeared completely in a minute, but on re-shaking appeared, but was not permanent. Another grm. of the soap, dissolved in 25 c.c. of the pint, was added, and on agitating a lather resulted, and had every appearance of being permanent. The mixture of magnesia and lime soaps was filtered on to a tared filter, washed with distilled water, and dried at 100° C.

Paper + insoluble soaps = 1·879 – 0·803 = 1·076 grms. CaO in soaps = 0·086 grm. = 7·99 per cent. Assuming that 100 parts anhydrous insoluble soaps = 130 ordinary soap, then soap destroyed per pint = 1·398 grms. = 21·5 grains = 172 grains per gallon = 24·5 pounds per 1000 gallons. As this water is actually in use on an industrial scale, 1000 gallons at least being used daily, it will be seen that the loss of soap per week through this cause must be considerable. It is not unusual to find waters of this degree of hardness being used on the large scale for washing operations.

Carbonate of lime, in suspension, causes hardness just as well as if in the soluble state. A cloudy suspension of $CaCO_3$ in CO_2 free water gave a hardness of 6° per 100,000. On adding a little more $CaCO_3$ the latter disappeared.

CO_2 by itself also causes hardness. Thus 10 c.c. saturated CO_2 added to 40 c.c. distilled water (free CO_2) required 6 c.c. for permanent lather. These lathers are always very feeble.

Soap solution is not a reliable standard for determining the amount of CaO present in very weak lime water, as will be seen from the following.

Grains per gallon of CaO in distilled H_2O :—

13·4, 13·4, 6·7, 6·7, 3·3, 3·3, 3·3.

C.c. soap required to lather 70 c.c. of above :—

17·0, 17·5, 13·0, 13·0, 12·0, 12·5, 9·5.

It is remarkable that these lathers only persist for two or three seconds, whereas natural waters as rich as these in lime will, generally, give permanent lathers. In all cases where the lather does not persist, or is very weak, it is a good plan to add a little NH_4Cl, which has usually the effect of making the otherwise feeble lather strong. I have never found this to interfere with the accuracy of the test, and have always found it to be of the greatest advantage.

BLANK TESTS.

So long as "blind tests" or "blanks" are necessary evils, it is important that they should actually indicate the correction which must be applied to analytical results to account for impure reagents.

It would seem that so apparently simple a matter could be settled off hand once and for all; but when the element to be estimated exists only in hundredths of 1 per cent—less in amount mayhap than is introduced by the reagents, then the method of determining the blank is of some moment.

Take the estimation of sulphur in steel, for instance, by the aqua regia and barium sulphate process. It is well known that the purest acids obtainable are never perfectly free from sulphur, and equally well known that an error of from 0·005 to 0·01 per cent would considerably enhance or deteriorate the value of high class bar-iron.

Arnold ("Steel Works Analysis," p. 99) advises that the usual volume of acids should be passed through the ordinary operations—which includes baking on the hottest part of the plate for at least half an hour—with a pinch of Swedish bar-iron "to fix the sulphuric acid as non-volatile sulphate of iron." Blair ("Chem. Anal. of Iron," p. 65) makes no mention of the "blank," but remarks that in the actual analysis "Carbonate of sodium is to be added to prevent any possible loss of sulphuric acid, which might otherwise occur by the decomposition of the sulphate of iron at a high temperature." N. W. Lord ("Notes on Metallurgical Analysis," p. 51) justifies the same procedure with still greater emphasis—" as the sulphates of iron are easily decomposed by heat."

Generally descriptions of this process do not refer to the necessity for a "blank." It is very common, however, to proceed as Prof. Arnold does, but substituting a little soda carbonate for the Swedish bar-iron.

Without discussing the merits of the separate means of fixing the sulphuric acid, it may be pointed out that neither way is really satisfactory, because they do not even approximate to the conditions under which the barium sulphate is ordinarily obtained. Where the amount of sulphur in an iron is exceptionally low, and the blank unusually high, the subtraction of the blank obtained as above may leave a negative result.

The following procedure, which has been acted upon for eight or ten years, and of which no published account has yet been seen, is offered as affording a close approximation to empirical accuracy in the determination of this and similar blanks :—

Take two separate amounts of steel weighing A and 2A grms. respectively, and by the usual process obtain from each the sulphur as barium sulphate. Then—

$BaSO_4$ (A) = $BaSO_4$ in A grms. Fe + blank (1)
$BaSO_4$ (2A) = $BaSO_4$ in 2A grms. Fe + blank (2)
(1) × 2 = 2$BaSO_4$ (A) = $BaSO_4$ in 2A grms. Fe + 2 blanks (3)
(3) – (2) = $BaSO_4$ due to blank.

Thus obtained the blank is usually lower than that obtained by evaporating the same volume of acids with a little soda carbonate.

J. T.

THINOLITE.

By ARTHUR M. EDWARDS, M.D., F.L.S.

Thinolite is a mineralogical "species," so-called; but what a species is exactly in this case it is difficult to understand; for I do not believe in species at all. Things can exist in forms which can be distinguished by sight one from the other; but what are "species," the different persons who view them differ themselves. In man, one man — the negro — is one species, and another divides the negro up into several species. So one calls thinolite a true species: another says it is a variety of Gaylussite. Mr. Clarence King, who named it, does not say why thinolite is a species, nor what a species is. But he named it from being formed on the shore of a lake, from the Greek name meaning a lake shore. It was a tuffaceous mineral, and he supposed it to come from Gaylussite, a mineral species. Gaylussite was named after the celebrated French chemist and philosopher, Nicolas Francois Gay-Lussac, and is a hydrous compound of carbonates of lime and soda. It occurs in crystals which are lengthened and prismatic. Their lustre is vitreous; the colour white, or yellowish white, and translucent. They have a composition of:—Carbonate of soda, 30·9; carbonate of lime, 33·8; and water, 30·3; and a specific gravity of 1·92 to 1·90. It has been produced artificially by mixing eight parts by volume of a saturated solution of carbonate of soda with one of a solution of chloride of calcium. It is well to remember this fact, as it bears directly on what I have to say anent thinolite. Perhaps thinolite is Gaylussite after all. It was named by the celebrated Professor James D. Dana. His son, Professor E. S. Dana, examined specimens for the U.S. Geological Survey, and stated that Gaylussite was confined to the name of one kind of the tuffaceous mineral found by King. So thinolite is a "variety" of the "species" Gaylussite. But why he distinguished thinolite as a species, unless it is crystalline—and Gaylussite is crystalline also, and the composition is the same likewise—I do not see. It is chemically the same as the other tuffas, and is included in the species which King refers to. But let that pass.

The possession of a specimen which was gathered for Bacillaria—or diatoms as they were called—at Salt Lake Desert, Utah, and for which I have to thank the Hon. A. A. Adee, of Washington, D.C., who got it from the Smithsonian Institution, contains that mineralogical curiosity—thinolite. And this warrants me in saying something on the subject of the Salt Lake Desert; for it is part of the Occidental Sea, as we will see. Besides, I have it from the Yellowstone Park, where it is recent and forming now. Miss Josephine E. Tilden, of the University of Minnesota, sent me the specimen; and I hope to have still more, for she went to that region again in the summer of 1898. And these gatherings, along with others which I have, confirm me in my theory of the Occidental Sea, of which I wish to speak now.

In 1878 King founded thinolite. The name Lake Lahontan was given by him to a great lake, the remains of which he found there. He supposed it to have been a lake in Quaternary times—at least it was a lake in that time, although it had existed long before, in the Eocene, before the Neocene. How far back the Eocene was is, of course, undetermined. It was in Nevada, and the remains exist now as Pyramid, Winemucca, Carçon, and Humboldt Lakes; these are salt lakes—the remains of Lake Lahontan. The region was covered with fresh water before the Glacial Period, which is the later part of the Pleistocene Period. It was a large lake or sea, which I call the Occidental Sea in the Eocene Period. It broke through the elevated edge of the basin by becoming larger in water, or by the elevation of the bottom. The Sierra Nevada was elevated later, and formed the Columbia and Colorado rivers flowing to the north and south; the Sacramento and San Juaquin rivers, which are in California, flowing north and south also, were formed then; and perhaps the upper Missouri river. The water was fresh, as is shown by the Bacillaria left there, and became more and more brackish until it resulted in the very salt lakes—more salt than the ocean. But it must be remembered and understood that this was in ancient times—Eocene or earlier periods. As the sea evaporated, the water remained fresh until it was frozen over in the earlier Glacial Period. The earth was thin there, for volcanic fires melted it underneath, and it sunk by the weight of the ice there, and cracked, and fire came out, and formed the melted rock that is now there in parallel lines from north to south—the faulted monoclines of the great plains. But it did not return to its original state; that is to say, it did not go down again, but crowded up the Sierra Nevada on the west. The bottom was thus elevated, when the which was melted and poured out; and the ice was melted, partly by the heated rock; and the waters flowed off, as I have said, by the Columbia and Colorado rivers. In this way we can account for the different deposits of Gaylussite and diatomaceous earth which is found there and on the Columbia river; the river cutting through it in deep gorges, or cañons as they are called. As the water evaporated, it left, as I have said, Lakes Lahontan and Bonneville, which were brackish; and it continued to evaporate until it left the very salt lake called Pyramid and others in the west, and Great Salt and Sevier lakes in the west.

And the diatomaceous earth is siliceous, not silica at all, but a hydrate which is soluble in fresh and also in salt water; and is the solid material which is present as Gaylussite a "species," or thinolite a "variety."

Gaylussite or thinolite can be and is forming now in Yellowstone Park, and the Bacillaria which are living now are the descendants of the same Bacillaria which we find in the Neocene rocks of Monterey, California, and likewise in the diatomaceous earths of the Great Plain. We can also see them in the Neocene diatomaceous earths of the world, from Jutland, Denmark, to Oran, Africa, and from Atlantic City, New Jersey, to Tampa Bay, Florida.

The fresh-water Diatomaceæ are sources of silica very valuable in various uses besides the mere making of polishing powder, for which they are extensively quarried. But they are the Eocene rock which I years ago styled Sub-plutonic from the presence of volcanic tuffa there. And the Neocene Platonaceous rock has also come into use for various purposes.

VOLUMETRIC ESTIMATION OF VANADIUM IN PRESENCE OF SMALL AMOUNTS OF CHROMIUM,

WITH SPECIAL REFERENCE TO THE ANALYSIS OF ROCKS AND ORES.*

By W. F. HILLEBRAND.

Outline and Limitations of the Method.

When chromium and vanadium occur together, and the former has been estimated colorimetrically, as detailed in a previous paper (*Journ. American Chem. Soc.*, xx., 454; Chemical News, vol. lxxviii., p. 227), the vanadium can in many instances be at once estimated without separating from the chromium by the well-known method of titration with potassium permanganate in sulphuric acid solution after reduction by sulphurous acid and expulsion of all excess of the latter.

The application of the method is subject to one limitation—the chromium must not be present above a certain moderate amount. This limitation is due to the considerable amount of permanganate required to produce a clear transition tint when titrating in a hot solution, as is necessary with vanadium. In a cold solution of chromic sulphate much less permanganate is needed to produce the peculiar blackish tint without a shade of green, which affords a sure indication of excess of permanganate, but in a hot and especially a boiling solution the oxidation of the chromium (Storer, through "Gmelin-Kraut," ii., [2], 290) itself takes place so rapidly that a very large excess of the reagent may be added before a pronounced end-reaction is obtained. Nevertheless, as will be shown, quite satisfactory determinations of as little as 1 or 2 m.grms. of vanadium pentoxide can be made in presence of as much as 30 m.grms. of chromic oxide.

Inasmuch as chromium is almost never a prominent constituent of the clays, coals, iron ores, and rocks in which vanadium has been thus far reported, the method promises to be of great advantage in rock and ore analysis, where these elements probably frequently occur together, generally with phosphorus and sometimes arsenic. It is not directly applicable in presence of molybdenum, and arsenic must first be removed by hydrogen sulphide if present.

Testing the Method.

A solution of sodium vanadate was prepared by fusing 0·937 grm. of pure vanadium pentoxide with sodium carbonate and diluting to 1 litre. Each c.c. contained 0·000937 grm. vanadium pentoxide. Of this, sufficient amounts were mixed with varying volumes of a standard solution of potassium chromate. After in some cases determining chromium colorimetrically, sulphuric acid was added, sulphur dioxide gas† introduced for a few moments, and the excess of the latter expelled by boiling in a rapid current of carbon dioxide, without which its complete expulsion is difficult. When cooled to from 70—80° C., the titration was made with very dilute solution of permanganate corresponding to about 1 m.grm. vanadium pentoxide to the c.c. as calculated from its

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* Read before the Washington Section, April 14, 1898. From the *Journal of the American Chemical Society*, xx., No 6, June, 1898.

† The direct use of a solution of sulphur dioxide or of an alkaline sulphite is inadmissible unless these have been freshly prepared, since after a lapse of time they contain other oxidisable bodies than sulphurous acid or a sulphite. The sulphur dioxide is best obtained as wanted by heating a flask containing a solution of sulphur dioxide, or of a sulphite to which sulphuric acid has been added.

TABLE I.

No.	Chromic oxide. M.grms.	Vanadium pentoxide. M.grms.	Vanadium pentoxide found. M.grms.	Error. M·grm.
1.	1	9·37	9·22	−0·15
2.	1	0·94	1·04	+0·10
			0·98	+0·04
3.	1·5	5·25	5·49	+0·24
			5·43	+0·19
4.	2	5·62	5·5	−0·12
			5·5	−0·12
5.	3	4·68	4·78	+0·10
			4·78	+0·10
			4·83	+0·15
6.	3	5·62	5·58	−0·04
			5·58	−0·04
7.	3·5	18·74	18 89	+0·15
			18·97	+0·23
8.	6	5·6	6·1	+0·50
9.	6	4·68	4·78	+0·10
10.	6	5·62	5·58	−0·04
11.	10	5·62	5·58	−0·04
12.	10	23·52	23·81	+0·29
			23·71	+0·19
13.	10	46·85	46·98	+0·13
			47·20	+0·35
14.	25	23·52	23·65	+0·13
			23 75	+0·23
15.	87·5	23·52	23·71	+0·19

TABLE II.

Showing application of Degree of Correction for Larger Amounts of Chromium, obtained by adding Potassium Permanganate to an Equal Bulk of Solution containing a like amount of Chromic Sulphate.

No.	Chromic oxide. M.grms.	Vanadium pentoxide. M.grms.	Vanadium pentoxide. found. Uncorr.	Vanadium pentoxide. found. Corrected.	Error. M.grm.	Volume of solution.
16.	20	0·94	1·59	0 99	+0·05	50—100 c.c.
17.	20	1·87	2·69	2·09	+0·22	,,
			2·39	1 79	−0·08	
			2·59	1·99	+0·12	
18.	20	18·74	19·4	18·73	−0·01	,,
			19·3	18·63	−0·11	
			19·3	18 63	−0·11	
19.	30	1·87	2·99	2·14	+0·27	About 100 c.c.
			2·79	1·94	+0·07	
			2·79	1·94	+0·07	
			2·69	1·84	−0·03	
			2 69	1·84	−0·03	
20.	30	1·87	2·69	1·79	−0·08	200 c.c.
			2·89	2·09	+0·22	
			2·89	2·09	+0·22	
			2·79	1·89	+0·12	
21.	62	46·85	48·60	47·60	+0·75	200 c.c.

TABLE III.

No.	Chromic oxide. M.grms.	Vanadium pentoxide. M.grms.	Vanadium pentoxide found. M.grms.	Vanadium pentoxide. Error. M.grm.
22. (Five grms. iron ore)	7	6·76	6 81	+0·05
			6·48	−0·28
			6·43	−0·33
			6·37	−0·37
23. (Five grms. iron ore)	3	3	3·08	+0·08
			3·13	+0·13
			3·03	+0·03
			3·08	+0·08
24. (Two grms. silicate)	1·6	1·87	1·86	−0·01
			1·97	+0·10
			2·07	+0·20
			1·86	−0·01

equivalent in iron. By repeating the reduction and boiling, any number of check tests can be rapidly made in the same solution. The solutions ranged in bulk from 50 to 200 c.c., according to the amounts of chromium added.

With the larger chromium contents the differences in the quantity of permanganate used, according as titration was effected at practically boiling temperature or a somewhat reduced one, were very apparent. In one case, at nearly boiling heat, 10 m.grms. of chromic oxide were largely oxidised to chromium trioxide, as shown by the change of colour from dark green to yellow. Even at 70—80° with this amount of chromium the results for vanadium will be too high unless the precaution is taken to ascertain the needed correction by adding permanganate to an equal bulk of hot chromic sulphate solution containing approximately the same amount of chromium. When this is done, however, the results are satisfactory even when as much as 30 m.grms. of chromic oxide are present and only 1 or 2 m.grms. of vanadium pentoxide.

Doubtless the modified iodometric method of T. Fischer (" Inaugural Dissertation," Rostock, 1894, p. 33) will in general give sharper results where chromium is present in considerable amount, and if so it should be preferred to titration by permanganate. But its use involves the preparation of a standard thiosulphate instead of the ever ready permanganate solution, and the manipulations are more time-consuming. The object has been in the present case to reach satisfactory results with the greatest expedition, and when chromium is not present in considerable amounts this is accomplished.

The accompanying tables contain the results of a considerable number of tests, those in Table II. being tabulated separately in order to show the degree of accuracy attainable with a large excess of chromium by applying the correction above mentioned, and also the amount of this correction.

In spite of the fact that the correction in most of the trials of this last table represents a large proportion of the permanganate used, the results must be considered satisfactory in view of the small amount of vanadium present, and they show that the method in competent hands after a little experience affords trustworthy figures.

Testing the Method on Rocks and Ores.

The following table shows its availability for rocks and ores. Known amounts of both chromium and vanadium were added to an iron ore and to a silicate, both free from arsenic, which were then fused with sodium carbonate and nitrate and further treated as follows:— After extracting with water and reducing manganese by alcohol, the silica and alumina were mostly removed by nearly neutralising with nitric acid and evaporating to near dryness. The washed precipitate was ignited and treated with hydrofluoric and sulphuric acids, the residue fused with sodium carbonate, since it frequently contains a little chromium, and again nearly neutralised, &c. To the combined and slightly alkaline filtrates was added mercurous nitrate, the precipitate of phosphate, vanadate, chromate, and carbonate was ignited in platinum, fused with a little sodium carbonate, leached with water, and filtered into a small graduated flask. After colorimetric determination of the chromium, sulphuric acid was added; both chromium and vanadium were reduced by sulphur dioxide gas, and the titration carried out as described.

These and other experiments show that, by taking not over 5 grms. of ore or rock, vanadium, if present to the extent of 0·01 or 0·02 per cent, can be readily estimated by exercising reasonable care in all the operations. Absolute confirmation of its presence can be easily obtained by evaporating and igniting the solution to remove excess of sulphuric acid, taking up with a few drops of dilute nitric acid, and adding to the solution in a test-tube a drop or two of hydrogen peroxide. In this way positive or negative assurance as to the presence of vanadium is given when the result of titration alone might be uncertain. Addition of ether at the same time affords a simultaneous test for chromium by its blue colour, and this might perhaps be made use of, if necessary, to remove all or the greater part of the chromium prior to titration of the vanadium, since the oxidation product of the latter does not dissolve in the ether.

It is even possible that the dark brown colour produced by hydrogen peroxide might be utilised for an exact colorimetric method for estimating vanadium.

THE SOLUTION OF SOLIDS AND LIQUIDS IN GASES.

By P. VILLARD.

THE phenomenon of the solution of a solid in a liquid—of a metallic salt in water, for example—consists of a change of state, of a veritable fusion in fact, by which the solid is enabled to become intimately mixed with the solvent liquid. There is nothing to prevent us generalising this notion, and admitting that every fluid, gas as well as liquid, can by its action on solid or liquid bodies which may be plunged therein, bring this body to a physical state in which they will become mixed, or in a word dissolved to a greater or less degree. Such a supposition is the more acceptable as the possibility of passing without transition from the solid to the gaseous condition has been proved long ago.

Experiment shows that gas possesses, with regard to both solids and liquids of little volatility, a dissolving power sometimes very considerable. If this power is not generally recognised under ordinary conditions, it is only due to the slight density of the gas compared with that of even the lightest liquids.

The first experiments relating to this question gave very distinct results. In 1880 Messrs. Hannay and Hogarth observed the solution of bromide of potassium, iodide of potassium, and chloride of iron, dissolve in the vapour of alcohol heated to +375° under pressure,—that is to say, at a temperature at which alcohol can only exist in the state of vapour, for it is then above its critical point. The same year M. Cailletet dissolved liquid carbonic anhydride in compressed air.

These first results give a valuable indication, showing that the power of dissolving does not belong exclusively to liquids. Without even speaking of its possible applications, there is a theoretical interest to be found in studying the phenomena of solution under such novel conditions, and with solvents whose constitution is more simple than that of liquids.

The experiments we have just referred to were made either at a high temperature or by using, as the body to be dissolved, a gas liquefied by pressure,—that is to say, a liquid of extreme volatility. These are not the only experiments which have been made in this direction; but no one appears to have tried whether, at the ordinary temperature, gases possess the property of dissolving bodies which are under ordinary conditions solid or liquid. Such a property, however, exists, and it is easily shown; it suffices to use compressed gas; the pressure, further, only appears to have an indirect influence on the phenomenon, viz., in increasing the density of the fluid.

I here give the results obtained at about +17°, except when otherwise stated, with gases for the most part permanent at this temperature.

I. *Oxygen, Air, Hydrogen.*

It is easy to watch the solution in oxygen of a liquid such as bromine, the vapour of which is coloured. It suffices to place a drop of bromine at the bottom of a narrow glass tube, and to pass in oxygen by the upper end; the oxygen must be compressed to about 200 atmospheres. The bromine vapour is first of all dispersed, but collects again near the liquid, but at the same time the colour becomes much more intense; diffusion then gradually takes place, and the colouration eventually fills the whole interior of the tube, the atmospheric contents of which presents a much deeper tint than before the compression.

The same result is obtained more rapidly by slanting the tube until it is almost horizontal; the gaseous layer, rendered more dense by its admixture with the vapour of bromine, spreads out and then diffuses all along the tube, to be replaced by still pure oxygen, on contact with which the liquid gives off more vapour, and in a very short while the colouration of the gas becomes uniform. The intervention of compressed oxygen has had the effect of turning a notable quantity of bromine into gas, which is added to the vapour already present in the apparatus, and of considerably increasing its density. This action is comparable with that exercised by a liquid on bodies which it dissolves—it is, in fact, a phenomenon of solution. When the pressure is diminished (the variation of pressure should be slow, so as not to sensibly affect the temperature), the colour becomes fainter, and at the same time small drops of bromine are deposited on the surface of the tube; thus we get the opposite of the previous experiment. These drops disappear again if the pressure is increased, and the colour of the gas becomes as deep as before. The solution of a very appreciable amount of bromine in compressed oxygen is thus made quite manifest.

Towards 300 atmospheres the colouration obtained far exceeds that of bromine water; it is practically the same as with six or seven times the thickness of ordinary saturated vapour of bromine,

It is, however, not necessary to have recourse to such great pressures to observe the phenomenon. The effect produced by oxygen is noticeable after a pressure of 4 atmospheres is reached, and is very marked at from 50 to 100 atmospheres. Under this last pressure the density of the dissolved bromine appears to be about three times the density of saturated bromine vapour *in vacuo.*

Air behaves in a very similar manner to oxygen; however, everything else being the same, the colouration obtained is a little fainter.

Iodine is also dissolved in oxygen in sensible quantities, but the phenomenon is not easily seen until the pressure is over 100 atmospheres and in tubes of at least 5 m.m. in diameter.

Hydrogen, which is both the lightest gas known and one of the most difficult to liquefy, only possesses a very feeble dissolving power; it can, however, be observed with bromine at pressures of 200 to 300 atmospheres.

II. *Formene.*

Formene is a very convenient body for dissolving notable quantities of liquids such as chloride of ethyl, sulphide of carbon, alcohol, or solids like camphor or paraffin. With this solvent it is not necessary to use very great pressures to show that the solubility of a liquid or of a solid in a gas may be as great as when using a liquid solvent. Thus chloride of ethyl dissolves in five or six times its volume of formene compressed to 180 atmospheres; at 200 atmospheres, at about 17°, the quantity of chloride that can be dissolved is such that the two fluids become miscible in any proportion, and the surface of separation between the liquid and the gas disappears. The same phenomenon is produced with sulphide of carbon towards 550 atmospheres at the ordinary temperature and at only 250 atmospheres at +150°.

Iodine is easily soluble in formene, to which it gives a lovely violet colour, which is very intense at 300 atmospheres even when examined through a thickness of only 2 m.m. We can also dissolve camphor and paraffin, and that in very noticeable quantities even with only $\frac{1}{2}$ a c.c. of compressed formene,—that is to say, less than a decigrm. On removing the pressure these bodies are deposited; the iodine and camphor crystallise on the surface of the tube, paraffin gives rise to a more or less abundant crop of brilliant flakes throughout the tube.

III. *Ethylene.*

Iodine dissolves in ethylene in sufficient quantity to colour it a very deep violet through a thickness of 2 m.m., at about 300 atmospheres. If this solution is allowed to stand for an hour or two it loses its colour, on account of the combination of the iodine with the ethylene; the iodide of ethylene formed remains in solution; when the pressure is released it is deposited in crystals, which are again dissolved if the pressure is re-established. Above 150 atmospheres ethylene dissolves paraffin abundantly; on removing the pressure the latter resumes the solid state, and forms a kind of felted mass throughout the tube.

Ordinary stearic acid is also dissolved, but in much less quantity than paraffin.

Camphor gives rise to a special phenomenon: if the pressure is moderated it immediately assumes the gaseous state, as with formene; if, on the contrary, the pressure reaches 150 atmospheres, the undissolved camphor becomes liquid, and then dissolves in the gas when this pressure is exceeded. The same phenomena take place in the inverse order as the pressure is released: there is first deposited a liquid formed of camphor and ethylene; at 150 atmospheres this liquid becomes solid; the camphor deposited below this pressure takes the solid state without transition.

IV. *Protoxide of Nitrogen, Carbonic Acid.*

Bromine dissolves in protoxide of nitrogen at 20 atmospheres, in the same manner in which it dissolves in oxygen at about 40 atmospheres. Compressed carbonic acid sensibly dissolves iodine, taking a violet colour. The dissolving power of these gases which can be liquefied at the ordinary temperature does not appear to be in any way extraordinary. But the pressures which can be obtained are limited by the liquefaction of the gas, at least if we do not exceed the critical temperature.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

THE BANQUET TO PAST PRESIDENTS.

Professor Dewar, F.R.S., President, in the Chair.

(Concluded from p. 289).

"The Foreign Members."

Sir William Crookes—"If it is possible for an after-dinner speaker to associate the word pleasure with the duty he has to perform, then I may lay claim to a slight feeling of that kind; for we are here assembled to do honour to our Past-Presidents, who are, as it were, now celebrating their jubilee in the Chemical Society. But it so happens that I also have a little jubilee of my own at this time, for exactly fifty years ago I made my first step in science by entering the Royal College of Chemistry. I remember as if it were yesterday, on a dull November morning, being introduced to Hofmann, who forthwith installed me at a bench, and asked Spiller, who was a few weeks my senior in science, to put me through the gases, preliminary to a course of the 'Giessen Outlines.' These were the days of compound ammonias, and heating in sealed glass tubes under pressure: having a certain facility at the blowpipe, I used to seal up some of these tubes; many of them, I fear, burst, for I well remember Hofmann's quaint remark, while watching one of them with anxious eyes, 'I think, Mr. Crookes, it will now gradually commence to explode violently.'

"One of the great troubles of a long life is to see the friends of early days drop off one by one. Of those in the College when I entered, I know only of Abel, Buckton, Dent, Spiller, and one or two others. It is a special pleasure for me to be here to-night and join in doing honour to one of these—my oldest scientific friend—Sir Frederick Abel. But in these reminiscences I must not forget my duty. I am asked to propose the health of the Foreign Members of the Society. There is a little topsyturveydom about this arrangement. I am saddled with a burden to which I have only a doubtful right. Such a toast can only be proposed by a Fellow, but when, some time ago, I approached your senior Secretary in that capacity, he refused to regard me in this light, and said I could only dine among you as a visitor.

"But the occasion is so special that, as a visitor, outsider, or Fellow, it must always be a great pleasure to propose the toast of the Foreign Members. We have a large roll of Foreign Members on our list. They are very eminent men; and, as proof, I need only mention that on this special occasion they are so busy with scientific work that few are able to come to join us to-night. But we have amongst us one of the most eminent of Continental chemists—Professor Ostwald—whose name is a household word to us all, and I will ask him to take the burden of replying to this toast."

Professor Ostwald—"The task laid upon my shoulders is so heavy that I cannot bear it in a foreign language. I must ask you, therefore, to allow me to answer in my own. Als ich die ehrenvolle Einladung für den heutigen Tag erhielt, war ich sofort bereit zu kommen. Nicht weil ich eine grosse Zahl guter Freunde und werthvoller Dinge in London sehen konnte; ich kam um eine grössere Sache. Ich kam, um Zeugniss abzulegen von der Gemeinschaft der wissenschaftlichen Männer aller Nationen. Das Fest, welches Sie feiern, hat seinen Anklang in der ganzen Welt gefunden; die wissenschaftliche Internationalität bringt es mit sich, dass des heutigen Tages überall gedacht wird, wo Chemiker sind.

"Meine Herren! Die Wissenschaft ist ein Land, welches die Eigenschaft hat, um so mehr Menschen beherbergen zu können, je mehr Bewohner sich darin sammeln; sie ist ein Schatz, der um so grösser wird, je mehr man ihn theilt. Darum kann jeder von uns in seiner Art seine Arbeit thun, und die Gemeinsamkeit bedeutet nicht Gleichförmigkeit. Wir werden immer an unseren französischen Arbeitsgenossen die Klarheit ihrer Darstellung und die Strenge ihrer logischen Entwickelung bewundern. Die Originalität der Gedanken und die unwiderstehliche Energie ihrer Durchführung wird stets die englische Forschung auszeichnen, und wenn wir Deutsche 'durch die Welt mit allen Sinnen schweifen,' um für unsere Arbeit eine möglichst breite Unterlage und einen möglichst weiten Horizont zu gewinnen, so thun wir darin auch nur, was unserer Natur entspricht.

"Hierzu möchte ich aus unserer Wissenschaft ein Beispiel entwickeln. Es ist ein wichtiges Resultat der heutigen Forschung, dass es nicht möglich ist, einen absolut reinen Stoff herzustellen. So rein er auch wird: die letzten Spuren seiner Mutterlauge können nicht entfernt werden, und er trägt immer ein Zeugniss seiner letzten Geschichte mit sich.

"Nun, meine Herren, in der Chemie des Geistes gilt ein ähnliches Gesetz. Auch der klarste Gedanke, die durchgearbeitetste Theorie trägt Spuren der Umgebung mit sich, aus der sie entstanden ist. Wenn nun der Fremde den neuen Gedanken zum ersten Male zu Gesicht bekommt, und er gefällt ihm nicht, so wird er sich zunachst nicht bewusst sein, ob der abstassende Eindruck von dem Gedanken selbst, oder von der anhängenden Mutterlauge herrührt, und es kann kommen, dass er ihn verwirft, nicht wegen seiner eigenen Beschaffenheit, sondern wegen zafälliger Beimengungen. Wenn ihm aber jenes *Gesetz der geistigen Mutterlauge* bekannt ist, so wird er sorgfältiger prüfen, und manches Vorurtheil, welches die gameinsame Arbeit der Nationen stört, wird fallen.

"Für diese Gemeinsamkeit bietet gerade der heutige

Abend einen ausgezeichneten Beleg. Als ich die Geschichte meines besonderen Gebietes, der Verwandtschaftslehre studirte, fand ich aus sehr früher Zeit eine Reine hochwichtiger Arbeiten, durch welche eine Anzahl fundamentaler Thatsachen festgestellt wurden. Die Arbeiten trugen den Namen des Dr. Gladstone. Ich habe vergeblich darauf gewartet, dass heute Abend diese Arbeiten erwähnt würden. Es ist nicht geschehen, und ich glaube, Dr. Gladstone hat selbst, vergessen, dass er sie gemacht hat. Aber wenn er sie auch selbst vergessen hat, die Wissenschaft wird sie nie vergessen. Und wenn jetst nach soviel Jähren, die Wissenschaft in Schweden, Holland, und Deutschland den Faden dort weitergesponnen hat, wo Dr. Gladstone in England ihn aus der Hand gelegt hat, so haben Sie ein schlagendes Beispiel vor sich, wieweit über Raum und Zeit die wissenschaftliche Gemeinsamkeit aller Forscher reicht."

"The Learned Societies."

Lord Reay—"I have seldom had the honour of proposing a toast to so distinguished an assembly, and at the same time a toast which, whether it was proposed at St. Petersburg, at Berlin, in Paris, in Vienna, or in Rome, coupled with the names with which it is coupled to-night, would attract the same applause. Lord Lister has conferred on the House of Lords, in entering it, an additional dignity. If we are asked—and we are occasionally asked—why there is a House of Lords, I do not know that we can give any better answer than by saying that the House of Lords is the proper place for receiving the princes of science. And, gentlemen, among the characteristics of the House of Lords there is one to which I shall allude,—one which I consider a very important characteristic. If I ask what are the characteristics of the House of Commons,—what are the characteristics of those who wish to enter the House of Commons,—then I am told that the catechism to which one has to answer is, 'Are you sound on Labour?' Now I am not quite sure that I fully grasp what is meant by soundness on Labour. But the problem may be solved when the House of Commons approaches a task which I know would tax the efforts of all the learned societies in London to deal with—the question of old age pensions. What is the catechism of the House of Lords? I think the question would be, 'Are you sound on Science?' I believe the House of Lords is sound on science, and in the contests of the future between prejudice and the laws of science, I think you will find, as you have found in the recent debate on vaccination, that the House of Lords will be on the side of Science, and not on the side of prejudice. And if the House of Lords is to remain sound on Science, then it will be due to having in its midst men like my noble friend Lord Lister, to keep it straight whenever it may show any inclination to diverge from the dictates of Science. There is hardly any subject at present in any department of the public service in which the question of science does not play a prominent part. And I do not believe that there is any department of the public service which does not occasionally seek the aid of a learned society on one or other of the scientific problems it has to solve. My late distinguished friend M. Léon Say used to predict of the twentieth century that Cabinets would be formed on the basis of sanitation. If so, we may still hope to see my noble friend Lord Lister at the head of the Home Office.

"With this toast is also coupled the name of my friend Professor Michael Foster. Mr. President and gentlemen, it is to me personally a great pleasure to couple with this toast that name, because the future of scientific education in London is committed to the care of Professor Michael Foster. The Statutory Commission, I hope, will set at rest that interminable controversy about the re-constitution of the University of London, and to Professor Michael Foster will fall the duty of settling the future of Science in that institution, which will influence the future of Science in our great empire. Let me conclude with an observation which is the result of what fell from the eloquent lips of the gentleman who last addressed us. He has spoken of 'die wissenschaftliche Internationalität.' I heard those words with great pleasure. Whatever causes of discord may disturb international relations, it will be among the great features of the work of the Learned Societies that they will always entertain cordial relations with the learned men in all foreign countries. And, Mr. President and gentlemen, whatever may happen on the banks of the Nile, of this I am sure, that the cordial relations which have existed between my distinguished friend Professor Ramsay on the banks of the Thames, and Monsieur Berthelot, on the banks of the Seine, will remain the same and tend to knit together that which ought never to be separated if the progress of civilisation is not to be interrupted. I give you the toast of 'The Learned Societies,' coupled with the names of Lord Lister and Professor Michael Foster."

Lord Lister—"Scientific men are not by any means always learned. Their devotion to their special studies often prevents such an occurrence. Nevertheless, I take it that in this toast the Learned Societies are understood to mean the scientific societies, and chiefly those of this metropolis. On this understanding, it seems to me very natural that the person who is asked to respond to this toast should be a representative of the Royal Society, because that Society is the mother of all the scientific societies in London; and while, if I may be allowed to say so, she is herself vigorous and active, she takes a deep maternal interest in the welfare of her offspring. Of her numerous progeny, none, I conceive, discharges her functions more healthily and efficiently than she who is this evening honouring some of her most illustrious and venerable sons. Among these it has been my joy to see my old teacher the venerated and beloved Professor Williamson. The Royal Society, I believe, does good to her daughters, stimulating them to work, and encouraging fruitful intercourse among them: witness, for example, the discovery of argon by the co-operation of Lord Rayleigh and Professor Ramsay. Mr. President, I received from one of your Secretaries an intimation that brevity would be the most valuable quality in any remarks I might make this evening. I gladly act on that suggestion, and will only now tender to you and your Council, on behalf of the representatives of scientific societies, other than the Chemical Society, present here this evening, our warmest thanks for the privilege you have given us of taking part in this memorable celebration. I would also thank Lord Reay for the exceedingly kind terms in which he has proposed the toast, and this illustrious company for the cordial manner in which they have received it."

Professor Michael Foster—"I feel deeply grateful for the very kind words in which Lord Reay has referred to me and my possible future services, in which I trust he may not be disappointed, and for the kind way in which you have received the toast. I perceive the delicate compliment to my physiological acquirements in the inference that, although a President as yet unborn, I can speak. I did not know, in accepting office, that the sweets of office would come thus before their time. I trust that they will be taken off, so to speak, at the other end of the bill. But remembering that all premature utterances, whether vocal or other, are feeble, the more feeble the more premature they are,—and it seems to me that, as President of the British Association, I was conceived the other day,—though I would have wished had not this premature deliverance been coupled with great lateness of the hour, to have turned from an uncertain and dim future to a rich and full past, and to have said something of my experience of these six great men, all of whom I can call my friends, and one of whom—Williamson—taught me not only chemistry but science, I will content myself in saying this, that though I do not know what may be before me as President of the British Association,—do not know what lions, true lions, false lions, there may be in my path,—I will do my best to make my tenure of office worthy, not only of the Association, but of Science. And may I also give utterance to this wish, in continuance of that international science of which my brother Ostwald spoke, that when the British Association meets at Dover, and the French Association meets at Boulogne, we shall feel that Fashoda is past over, and that we shall not be using the resources of science to make each other as small as we can, but that each will be using the strength of the other to advance the resources of a common knowledge."

"The Guests."

The Treasurer—"I have the honour to propose to you, Fellows of the Chemical Society, that you should drink to the health of your guests. We are favoured here to-night with the presence of a large and distinguished body of gentlemen; how large, and how distinguished, you yourselves may know by a mere glance at the list of their names which is already furnished to you. We are deeply grateful to these gentlemen for the way in which they have responded to the invitation of the Society to be present here to-night to do honour to the gentlemen who are our special guests. Large as the number is, we could well have wished that it was still larger; for our hospitality and our welcome have their physical limits only in the capacity of this room. We could well have wished, for example, that a greater number of our Foreign Fellows were here present. You have heard from the President many messages of congratulation and of good will from certain scientific organisations abroad, and from individual Fellows of our Society. But these messages by no means account for all the kind words, for all the utterances of friendship and felicitation, which have been made in reference to this occasion. I have recently passed through many Continental capitals, and have visited incidentally a number of academic centres, and I have had the pleasure of meeting a considerable proportion of those gentlemen whom we are proud to number amongst our Foreign members. Thus, I have met Franchimont at Leiden, Cleve at Upsala, Waage at Christiania, Pettersson and Arrhenius at Stockholm, Emil Fischer, Landolt, and van't Hoff at Berlin, Liebermann and Witt at Charlottenberg, Ladenburg at Breslau, our active collaborateur Brauner at Prague, our old friend Debus in Cassel, and last, but not least, the *doyen* of the illustrious body, my venerated teacher Bunsen, at Heidelberg. And, gentlemen, I am charged by each and all to convey to you, should I have the opportunity, their heartfelt congratulations on this occasion, and their great regret that circumstances should have prevented them from being here to testify by their presence their appreciation of the great services which these gentlemen whom we especially delight to honour to-night have rendered to Science, and to the Society of which we are so thankful to see them still members. I should like to say an additional word or two about Bunsen. His Excellency has learned to grow old gracefully. He bears the weight of his eighty-eight years admirably. His deafness, it is true, has somewhat increased, and he complained with a touch of pathos which, under the circumstances, has just a suspicion of the element of comedy, that 'he begins to find that his eyesight is not so good as it used to be.' It was for this reason that he asked to be excused from conveying in writing the message which he wished me verbally to transmit to you. I am asked to associate with this toast the name of Mr. Haldane and that of Dr. Böttinger. Mr. Haldane is known to all here for the admirable part he has taken in furthering a cause which many of us have very near at heart—that is, the advancement to its legitimate position of our Metropolitan University. Dr. Böttinger is known to many here as a leading member of a firm whose name is as a household word in the mouths of those who speak of the material and industrial triumphs of our science. Gentlemen, without further word, I give you the health of 'Our Guests,' and I associate with that toast the names of Mr. Haldane, Q.C., M.P., and Dr. Böttinger."

Mr. Haldane—"I confess I feel a little shy in uttering the few sentences which I have to address to you. Previous speakers have come before you with a wealth of distinctions and a profusion of academic tone which it is impossible for me to imitate. Lord Reay, who represents a different branch of the Legislature, has put me to shame by telling me that the House of Lords is 'sound on science.' Well, I am glad to hear it, and I wish I could say as much for the House of Commons. I cannot speak to you as a man of science, nor as a representative of any department of abstract knowledge; I can only speak to you as a humble—that most humble of all functionaries—unofficial member of an Opposition, or what I fear some of you will consider, a battered and shattered fragment of a still more battered and shattered Party. I do not admit, needless to say, the impeachment. I do not regard myself in the least as an atom which has got outside its proper molecule. There is plenty of potential energy in my political combinations. When I was at the University of Göttingen, there was a song we used to sing which ran 'Die Philister sind uns gewogen meist.' Even members of the House of Commons acknowledge the deep debt they are under to-day to science, and perhaps most especially to chemical science. Gentlemen, there was a great victory won the other day in the Soudan. That victory was due to the forethought and skill of a very distinguished soldier; but also to another force. That victory, which pronounced once for all, and finally, the supremacy of mind and trained skill over the most powerful of savage combinations; that victory was won, not merely on the fields before Omdurman, but in the laboratory and the workshop. The smokeless powders, the modern rifling, the bullet of most recent construction, all these are your work. But the obligations which you have rendered us in the past are as nothing to the obligations to which some of us look forward to you in the future. We have spent money lavishly, without a word of complaint from the taxpayer, on the support of the Army and the Navy; but we have not yet spent the money which I believe we ought to spend, and shall be forced to spend, upon the defence of our industries. The country from which Professor Ostwald comes can teach us a lesson. In Germany, where 70 per cent of the upkeep of the universities comes from the Government, they have taught us how to put mind into our work. There are men who would gladly convert the British public to it, but their work is yet to be done. We shall realise these things when the House of Commons will vie with the House of Lords in giving predominance to the great task of diffusing scientific knowledge among our commercial men as among our soldiers. It is with that sentiment in my mind, with that feeling of obligation to these pioneers of the work of the members of this Society, that I gratefully thank you for the toast which has been proposed."

Dr. Böttinger—"Allow me also to thank you most heartily and sincerely for the great honour you have conferred upon your guests by your kind invitation, and by putting them in a position to take part in this beautiful festival on the celebration of six Masters of English Science. Gentlemen, I may also thank you, most especially in my own name, for the great honour you have conferred upon me in mentioning my name specially among the toasts of the evening. I shall not forget this evening; it will always be in my mind a pleasant recollection of what Professor Ostwald said of you. In science we know no bounds and no boundaries internationally, for we are one great common nation. Your esteemed President, Professor Dewar, cordially remarked on the character of the messages you have received this evening from all parts of the scientific world. Allow me to add to these, and assure you that not only from the scientific world, but elsewhere, these feelings are shared with the same heartiness with respect to the great work these gentlemen have done for the development of science and for the benefit of the human race. It is for me a particular pleasure to see by the list of your numerous members and guests that you also acknowledge that science and industry and technique must go hand in hand; that we who reap the technical part must rely upon the men of science for new ideas and advancement of our work. But I believe and am convinced that the men of science in their connection with us also find new initiative for the furtherance of their ideas; they also find that in connection with the industrial and technical world they see what is further necessary for the development of their work. I am sure that the names of these six illustrious scientific men will be mark-stones in the world for the future, they will be stepping-stones for the new generations. Before I end, allow me to deviate from your English custom, and introduce a custom with us in Germany, a custom which is always followed with great enthusiasm, and to propose now the health of one whom particularly we have to thank for this beautiful evening: it is the health of a man who is a pioneer in science also, and has a great name. I need only remind you of liquefied air. I speak of Professor Dewar, and I ask you to join with me in a hearty three cheers for him. So take your glasses and join with me in our German fashion with Hoch! Hoch! Hoch!

The President—"My Lords and Gentlemen,—I must protest against the intrusion of an additional toast. We have had a most delightful evening; we have achieved our great aim; and I think that the present President is such a nonentity in comparison with the men we are here to honour, that the less said about him the better."

Letters, telegrams, and messages of congratulation were received from the following Foreign Members:—Professor Arrhenius, Stockholm; von Baeyer, Munich; Beilstein, St. Petersburg; Berthelot, Paris; Lecoq de Boisbaudran, Paris; Bunsen, Heidelburg; Cannizzaro, Rome; Cleve, Upsala; Curtius, Bonn; Erlenmeyer, Aschaffenburg; Fischer, Berlin; Fittig, Strassburg; Franchimont, Leiden; Friedel, Paris; Wolcott Gibbs, Cambridge, Massachusetts; Graebe, Geneva; van 't Hoff, Berlin; Körner, Milan; Ladenburg, Breslau; Landolt, Berlin; Liebermann, Berlin; Lieben, Vienna; Markownikoff, Moscow; Mendeleeff, St. Petersburg; Menschutkin, St. Petersburg; Moissan, Paris; Nilson, Stockholm; Pettersson, Stockholm; Rammelsberg, Berlin; Raoult, Grenoble; Remsen, Baltimore; Schlœsing, Paris; Spring, Liège; Thomsen, Copenhagen; Troost, Paris; Waage, Christiania; van der Waals, Amsterdam; Wislicenus, Leipzig; Witt, Charlottenburg, ans from a number of distinguished Fellows and friends of the Society.

A special vote of congratulation was passed by the Russian Chemical Society, and transmitted by Professor Mendeleeff.

"At a meeting of the Russian Chemical Society held this day, it was resolved, that the Society avail itself of the exceptional opportunity of being able to congratulate conjointly Sir Joseph Henry Gilbert, Sir Edward Frankland, Professor Odling, Sir F. A. Abel, Dr. A. W. Williamson, and Dr. J. H. Gladstone, whose distinguished services during half a century stand out as a model for all investigators in Chemical Science, and also express the wish to see the further results of their labours in the annals of Science for many years to come.

Hon. President, D. Mendeleeff.
Secretary, A. Gorboff.

St. Petersburg. $\frac{\text{20 May,}}{\text{1 June,}}$ 1898."

The following telegram was received from the German Chemical Society. "The sister Society sends both Jubilee congratulations and greetings to the Jubilee celebration of the Presidents of the Chemical Society, Gilbert, Frankland, Odling, Abel, Williamson, and Gladstone. The German Chemical Society, C. Liebermann, President."

PHYSICAL SOCIETY.

Ordinary Meeting, December 9th, 1898.

Mr. Shelford Bidwell, F.R.S., President, in the Chair.

Dr. C. Chree read a paper on "*Longitudinal Vibrations in Solid and Hollow Cylinders.*"

The ordinary formula for the frequency of longitudinal vibrations refers to an ideal rod of infinitely small section. This formula constitutes a first approximation, according to which the higher notes are exact harmonics of the fundamental note. Prof. Pochhammer and Lord Rayleigh independently, over twenty years ago, arrived at a corrective term for solid isotropic rods of circular section, according to which the harmonic relation between the notes is no longer exact. During the last twelve years Dr. Chree has devoted several papers to the subject, confirming by independent methods the *results* obtained by Pochhammer and Rayleigh, and arriving at analogous results for other forms of section, and for material symmetrical round an axis but not isotropic. The first part of the present paper develops what appears to be a new method, based on expressions obtained some years ago by the author for the mean values of the strains in an elastic solid of any kind or shape, exposed to any system of forces. Besides confirming his previous results, Dr. Chree obtains new results applicable to material neither isotropic nor symmetrical round the axis of the rod. The second part of the paper treats of a hollow circular rod, or tube, of isotropic material. When the walls of the tube are thin the correction to the ordinary formula is twice as large as for a solid rod of the same diameter. The different methods all point to the conclusion that the ordinary formula supplies a close approximation to the truth only so long as the greatest diameter of the cross section is small compared to the nodal interval in the rod.

A paper on the "*Thermal Properties of Normal Pentane,*" by Mr. J. Rose-Innes and Dr. Sydney Young, was then read.

In 1894 the authors investigated the relations between the temperatures, pressures, and volumes of iopentane, through a wide range of volume; the results are published in the *Proc. Phys. Soc.*, xiii., pp. 602-657. It is there shown that if a and b are constants depending on the nature of the substance and on the volume, the relation $p = (b\,T - a)$, at constant volume, holds good with but small error from the largest volume (4000 c.c. per grm.) to the smallest (1·58 c.c. per grm.). In the neighbourhood of the critical volume (4·266 c.c.), and at large and very small volumes, the observed deviations are well within the limits of experimental error, but at intermediate volumes they are somewhat greater. As they exhibit considerable regularity it is a question whether they could be attributed entirely to errors of experiment. In any case the above relation may be accepted as closely approximate to the truth. The present paper refers to a similar investigation on pure normal pentane obtained by the fractional distillation of the light distillate from American petroleum. The method employed for this separation is fully described in the *Trans. Chem. Soc.* (1897, vol. lxxi., p. 442); the vapour-pressures, specific volumes as liquid and saturated vapour, and critical constants, are given in the same Journal (p. 446). With regard to theoretical deductions from the present results, advantage is taken of the fact that a similar set of experiments had already been carried out with isopentane, which is an isomer of normal pentane. It was hoped that light would be thrown on the question of the influence exerted by difference of chemical structure on the thermal properties of a substance. The conclusion arrived at as most probable is that the coefficients of the second power of the density in the expansion of p must be different for the two snbstances. The slope of the curve obtained by plotting $(a\,v^2)^{-1}$ against $v^{-\frac{1}{3}}$ suggests discontinuity somewhere about vol. 3·4, as with isopentane.

Mr. Lehfeldt asked whether the authors had observed any other singularity or discontinuity at vol. 3·4. He also asked whether the authors were satisfied with ordinary squared-paper in plotting their curves. It ought to be possible to design a machine for doing the work mechanically to 1-50th of a m.m. accuracy.

Mr. Appleyard said the fractionating apparatus devised by Dr. Young was a great improvement on older forms; it ensured that there should always be sufficient, and yet not too much, liquid at each valve-trap. He hoped that details of the tube, in the latest form, would be included in the paper. In the separation of such a mixture as chloroform and alcohol, the common method by water-extraction was imperfect; it was not desirable always to convert the mixture wholly into chloroform. Ordinary fractionating tubes yielded an impure distillate in this case. Perhaps the difficulty was inherent for these two liquids. Dr. Young's apparatus would put the question beyond doubt.

Dr. Young, in reply, said that the only objection to curve-tracers was their cost. The curves he had obtained from his experimental results were all isothermals; he did not think isobars would indicate anything such as Mr. Lehfeldt had suggested. With regard to such mixtures as chloroform and alcohol the chances of separation were difficult to predict. A distinction might, however, be drawn between liquids partially miscible and liquids miscible in all proportions. Hexane (b. p. 69° C.) and benzene (b. p. 80° C.), for instance, were both hydrocarbons miscible in all proportions, and it might be thought possible to separate them by a fractionating apparatus; but experiment shows they cannot so be separated. If alcohol and chloroform should turn out to be miscible in all proportions, the probability was that they could not, effectively, be fractionated; if, on the other hand, they prove to behave like partially miscible liquids, the separation by fractionating apparatus such as he had described was rendered possible.

The President proposed votes of thanks to the authors, and the meeting adjourned until January 27th, 1899.

Auriferous Conglomerate of the Transvaal.—G. F. Becker (*Am. Journ. Sci.*).—The auriferous conglomerate of the Witwatersrand gold field constitutes the most important gold deposit ever known. A strip of country a couple of miles in width and about 30 miles in length has yielded since 1887 about 240,000,000 dollars, and only about one-fifteenth of the accessible gold has been extracted. The nature of this wonderful deposit is a subject of manifest interest to geologists and mining engineers, who, however, have arrived at various conclusions. No considerable doubt exists that the conglomerate is a marine littoral deposit, but some observers have held that the gold is detrital, being an original part of the conglomerate; others that it is a chemical precipitate from the ocean in which the pebbly beds were laid down: and still others that the precious metal reached the uplifted but uncemented gravel in solution, so that the ore-bearing strata are allied to ordinary veins. After presenting all the more striking facts which it is necessary to consider in testing the theories propounded to account for the deposition of gold on the Rand, the author rigidly tests each theory by the facts, and reaches the conclusion that the deposition of the gold was in no sense chemical, that there are no valid objections to the theory of marine placer origin, and that no noteworthy features are left unexplained by this theory. The argument is so clear and cogent that the detrital theory of the Transvaal gold may be regarded as firmly established.—*Journal of the American Chemical Society*, vol. xx., No. 9.

NOTICES OF BOOKS.

Technical Mycology: the Utilisation of Micro-organisms in the Arts and Manufactures. By Dr. Franz Lafar. Translated by C. T. C. Salter. Vol I. "Schizomycetic Fermentation." With 1 Plate and 90 Figures. Pp. 405. London: Charles Griffin and Co. 1898.

The excellent volume now before us deals entirely with bacteria, both useful and harmful, more especially with regard to fermentation in distilling and brewing, in the preparation of wines and vinegar, in dairy work and farming, &c.

This volume is divided into nine sections and thirty-eight chapters.

In the introduction, the theory of spontaneous generation is discussed, and we find the author seems rather inclined to the opinion that it is simply *unproven*, but not *impossible*.

The earlier chapters deal with the forms of growth, dimensions of bacteria, the structure and constitution of the cell, reproduction, germination, &c. There are three types of germination. In the first type, the spore gradually acquires the normal dimensions and functions of the vegetative form by absorbing liquid from the surrounding medium; it soon divides and reproduces by fission. In the second type, the contents of the spore elaborate into a new rod surrounded by a thin membrane, and eventually bursts the spore capsule at the point of least resistance at the poles; the capsule then shrinks at once to its original size and disappears by dissolving in the surrounding liquid. In the third type, the spore membrane does not burst at the poles, but along a line corresponding with the equator of the spore.

Section II. deals with the general biology and classification of bacteria. The mutual influence of two or more species may be of such a nature that it is impossible for them to live together—the presence of one species retarding the growth of, or even killing, the other. A number of examples of such cases are given throughout the book.

Section III. treats of sterilisation and pure cultures, and Section IV, with chromogenic, photogenic, and thermogenic bacteria. Some bacteria are capable of withstanding prolonged heating without being killed, such as the *Schizomycetes*, which can withstand boiling water for several hours. These, and various other kinds, are dealt with in Section V. The preservation of milk, meat, eggs, vegetables, and fruit is also thoroughly gone into. Lactic fermentation and allied decompositions form the subject-matter of Section VI.

Decompositions and transformations, such as the phenomena of putrefaction, the fermentation of cheese, and the fixation of free nitrogen by bacteria make up Section VIII. The discovery of leguminous nodules was one of very great importance to agriculture. These growths are now being cultivated artificially, and applied direct to the soil as manure.

Section IX., on oxidising fermentations, the iron, sulphur, and nitrifying bacteria, acetic fermentation, and the oxidases, brings the volume to a close

There is a copious table of contents, but we regret to see that there is no alphabetical index.

The preface, written by Dr. Emil Ch. Hansen, bears testimony to the discernment and ability with which the book has been compiled: we are glad to endorse the opinion therein expressed.

The Living Organism: an Introduction to the Problems of Biology. By Alfred Earl, M.A., late Scholar of Christ Church College, Cambridge; of the Inner Temple, Barrister-at-Law. London: Macmillan and Co., Lim. New York: The Macmillan Company.

The author, addressing himself to the student of biology, urges the importance of the science and its influence upon current thought, observing that "inaccurate conclusions and unsound speculation have more serious issues in the case of biology than in any other of the natural sciences," and as security against this, points out the necessity of great care in instruction in the rudiments, and warns the student against taking too much for granted. The character of the work is critical; and the real object, as stated by the author, is to direct attention to the important truth that, "though chemical and physical changes enter largely into the composition of vital activity, there is much in the living organism that is outside the range of these operations."

The subject is treated in a masterly manner, and will repay close perusal by one seriously entering upon scientific investigation in any of its branches, particularly those included under the name of biology.

The matter is not suitable for abstraction, but the concluding sentence is very characteristic of the whole:—"Every branch of research leads sooner or later to the unknowable, and that stage is soon reached in attempting to pursue the mechanical conception of life."

In the present volume, as in a previous work, great pains have been taken to impress the student with the value of thinking for himself.

The subjects are well and clearly arranged, and there is a good index.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvii., No. 11, September 12, 1898.

Crystallisation of the Anhydrous Sulphides of Calcium and Strontium.—M. Mourlot.—Proceeding in the same manner as for the preparation of crystalline barium sulphide, the author has succeeded in obtaining calcium and strontium sulphide, anhydrous and crystalline. A mixture of calcium or strontium sulphate and carbon, or the amorphous sulphide prepared according to Sabatier's method, is submitted to the action of the electric furnace. The crystalline sulphides thus obtained are more stable than the corresponding amorphous sulphides, and less easily attacked by the various reagents. Under the action of carbon at a very high temperature, they are converted into carbides.

A Double Carbide of Iron and Tungsten.—P. Williams.—When a mixture of tungstic acid, iron, and carbon are allowed to react on one another at the temperature of the electric furnace, the mass obtained has a metallic appearance, and is of a complex nature. It consists of carbide of tungsten (WC), probably a carbide (W_2C), and several double compounds of tungsten and iron, one of which the author has isolated and examined. This compound is separated from the whole mass by treating the latter with hot strong hydrochloric acid. The action is rapid at first, but falls off owing to the crystalline residue covering and protecting the bulk of the mass. Frequent grinding is therefore necessary. A crystalline powder is left, formed of two double carbides of iron and tungsten; the simple tungstic carbide and graphite. The double carbide can be separated by means of a magnet, it being highly magnetic. Analysis shows it to have the composition $2Fe_3C.3W_2C$.

Commercial Extraction of Thoria.—G. Wyrouboff and A. Verneuil.—The authors have already announced a very exact method for separating thoria from all the other rare earths which usually accompany it. This method, based on the use of hydrogen peroxide, led to a commercial extraction which is both simple, rapid, and cheap, since it extracts the whole of the thoria in a given mineral in a pure state. This method was applied to several tons of monazite, and gave very satisfactory results. The great advantage of using peroxide of barium is that the precipitated mass contains all the thoria and impurities which do not exceed one-third of its weight.

Constitution of Natural Earthy Substances.—G. André.—Nitrogen in the soil occurs in a soluble form, chiefly as nitrate. This is produced at the expense of so-called organic nitrogen under the influence of the nitric ferment and in presence of a base. Organic nitrogen proceeds from slow vegetable decay or the fixation of free nitrogen by certain micro-organisms. By treating vegetable earth either with alkalis or dilute acids, the nitrogenous matter can be gradually resolved into soluble form, and from the results obtained, Berthelot and André have concluded that the nitrogenous matter of the soil behaves like an amide. The author points out that this nitrogenous matter exists in many different forms, as the result of experiments on four specimens of earth. In order to obtain comparable results, a known weight of each substance is treated similarly, viz.:—(1) Treatment with caustic potash, and subsequent treatment of the insoluble residue with hydrochloric acid; and (2) the inverse process. The results of estimation of the nitrogen are tabulated as percentages of the total amount of nitrogen present in each of the original substances. From these numbers, deductions are drawn as to the ratio in which the different forms of nitrogen occur in the specimens analysed.

No. 12, September 19, 1898.

This issue contains no chemical matter.

Bulletin de la Société Chimique de Paris. Series 3, Vol. xix.-xx., No. 9.

The Solubility in Water of Tricalcic Phosphate and of Apatite.—Jules Joffre.—Already inserted.

New Method of Fractionating the Yttric Earths.—G. Urbain.—Already inserted in full.

Nature of the Didymium which accompanies Yttria from the Monazite Sands.—G. Urbain.—Already inserted in full.

On Neodymium.—O. Boudouard.—Already inserted in full.

Compound obtained with Nitrate of Mercury and Trimethylcarbinol.—G. Denigès.—Already inserted.

Preparation and Etherification of Dissymmetric Dimethylsuccinic Acid. — E.-E. Blaise. — Already inserted.

Action of Aniline and of Phenylcarbamide on the Ketonic Acids of the Series $C_nH_2N—10.O_3$.—T. Klobb.—A long paper, not suitable for abstraction.

Some Interesting Experiments on the Synthesis of Estragol and the Allylic Essences.—Ch. Moureu.—The author, with M. Tardy, heated over a water-bath iodide of allyl and anisol in the presence of powdered zinc. A violent reaction took place, and vapours of iodine were given off, and iodide of methyl, anisol, phenol, and a mixture of various other compounds passed over on distillation after treatment with dilute soda and being fractionally distilled. Between 200° and 210°, a liquid body is collected still containing traces of iodine, of which the elementary composition is sensibly different to that of estragol. The author then had recourse to the method of Friedel and Crafts, based on the curious properties of chloride of aluminium; and by the help of that method he obtained a small portion of a liquid having decidedly the smell of estragol, but the quantity was too small for further isolation.

Thermochemistry. Quinoleic Bases and Hydrides: Salts.—Marcel Delèpine.—Quinoleic bases are generally prepared by the action of a primary aromatic amine on an aldehyd, an acetone, or a substance susceptible of giving rise to one of these functions. Hydrogen is not given off; it either acts on the quinoleic base, forming a hydride, or on the aldehydic or acetonic body, or on an oxidising auxiliary used in the reaction. The author has studied this reaction from the thermochemical point of view, using quinolein, quinaldine, and their tetrahydrides. He has also studied the basicity of these compounds with regard to hydrochloric acid, and has obtained five compounds.

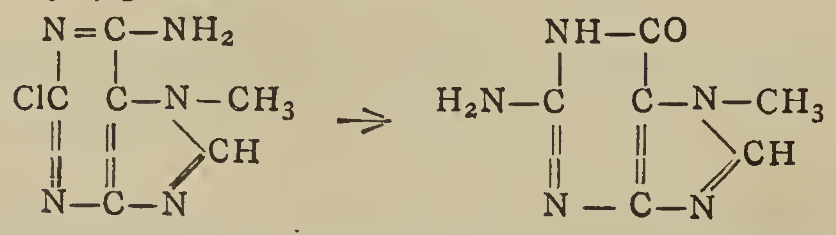
The Sugar in Orange-peel.—J. Flatau and H. Labbé. —Already inserted.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxi., March 28, 1898.

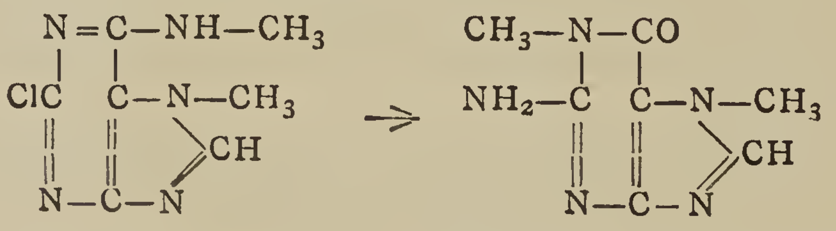
On Racemy.—A. Ladenburg.—The author has given the name of partial racemy to the following phenomenon. Salts which form certain acids enclosing an asymmetric carbon with active base, give by decomposition an inactive acid at certain temperatures and an active acid at other temperatures.

The Racemisation of Acid Malate of Ammonium. —J. H. van 't Hoff and H. M. Dawton.—Pasteur showed that when solutions of acid malate of ammonium are left alone at about 70° they deposit, first, crystals of active malate, and the mother-liquor then contains a hydrated racemic salt. Below 70° only racemic salts are obtained. The authors have determined the exact conditions of temperature, &c., under which this transformation takes place.

Molecular Transformation in the Group of Purines. —E. Fischer.—The author shows that warm dilute alkalies transform methyl-γ-amino-6-chloro-2-purine into methyl-γ-guanine—

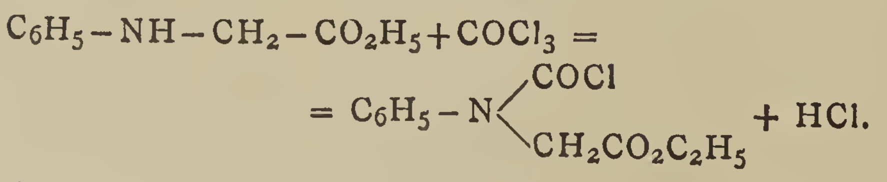


This reaction can be explained by an internal molecular transformation, but the author prefers to admit a momentary rupture of the nucleus. To prove this hypothesis he has effected the same transformation with methyl-γ-methylamine-6-chloro-2 purine and obtained the corresponing dimethylguanine—



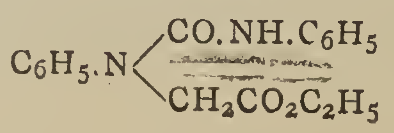
These reactions are easily done by heating the chlorinised derivative to 100° for two hours with a large excess of water and a small quantity of soda.

A Synthesis of Diphenylhydantoïn.—W. Hentschel. —Phenylhydantoïn was prepared by saturating a benzoic solution of phenylglycocol with $COCl_2$; this gives rise to a corresponding chlorocarbonate—



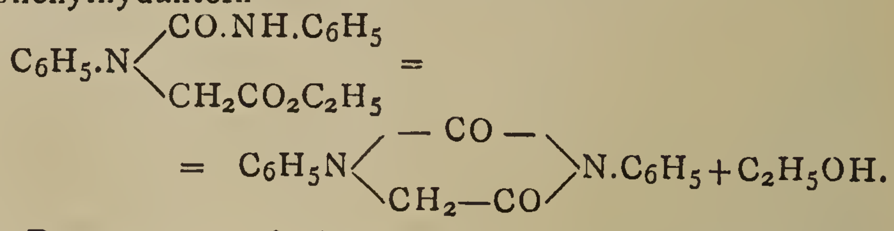
$$C_6H_5-NH-CH_2-CO_2H_5+COCl_3 = \\ = C_6H_5-N\left\langle\begin{matrix}COCl\\ CH_2CO_2C_2H_5\end{matrix}\right. + HCl.$$

Aniline reacts on this body when warm, giving—



$$C_6H_5.N\left\langle\begin{matrix}CO.NH.C_6H_5\\ CH_2CO_2C_2H_5\end{matrix}\right.$$

Repeated crystallisations transform this product into diphenylhydantoïn—



$$C_6H_5.N\left\langle\begin{matrix}CO.NH.C_6H_5\\ CH_2CO_2C_2H_5\end{matrix}\right. = \\ = C_6H_5N\left\langle\begin{matrix}-\;CO\;-\\ CH_2-CO\end{matrix}\right\rangle N.C_6H_5+C_2H_5OH.$$

Preparation of the Acetals of the Ortho-substituted Aromatic Aldehyds.—E. Fischer and G. Giebe.—In applying their process for the preparation of acetals to the *o*-substituted aromatic aldehyds, the authors have studied the influence of neighbouring groups on the speed of the reaction; the electro-negative radicals (Cl, NO_2, &c.) accelerate it slightly, and the electro-negative radicals (CH_3, &c.) retard it. They have prepared a number of acetals by leaving the aldehyd in contact with an excess of alcohol containing 1 per cent of hydrochloric gas for twenty-four hours; these acetals are all described and their formulæ given.

MISCELLANEOUS.

Coating Iron and other Metals with Lead.—E. v. Münstermann.—The object is first cleaned with a brush soaked in petroleum, then dried, and placed in a lead-lined bath containing dilute nitric acid. After drying, it is plunged into a mixture of sulphuric acid, urine, and water, and left until all trace of rust has disappeared. After this, the object is immersed in a mixture of hydrochloric acid, water, and double iodide of mercury and potassium, to facilitate the adherence of the lead. It is finally dipped in melted lead. For forged objects, the temperature of the lead bath should be at least 470° C.; but for castings it should be much higher.—*Ackermann's Gew. Zeit.*, xxiv., [3], p. 21.

Royal Institution.—The following are the lecture arrangements at the Royal Institution before Easter:—Sir Robert Ball, six lectures (adapted to young people) on "Astronomy"; Professor E. Ray Lankester, ten lectures on "The Morphology of the Mollusca"; Mr. A. Henry Savage Landor, three lectures on "Tibet and the Tibetans"; Dr. Allan Macfadyen, four lectures on "Toxins and Antitoxins"; Mr. William Poel, three lectures on "English Playhouses in the 15th, 16th, and 17th Centuries"; Sir Alexander Mackenzie, three lectures on Liszt, Tschaikowsky, Brahms" (with musical illustrations); The Rt. Hon. Lord Rayleigh, seven lectures on "The Mechanical Properties of Bodies." The Friday Evening Meetings will begin on January 20th, when a Discourse will be delivered by Professor Dewar on "Liquid Hydrogen"; succeeding Discourses will probably be given by the Right Hon. Sir Mountstuart E. Grant Duff, Mr. Victor Horsley, Professor H. S. Hele-Shaw, Mr. Richard R. Holmes, Sir Frederick Pollock, Bart., Professor H. L. Callendar, The Right Hon. Lord Rayleigh, and other gentlemen. The year 1899 is the Centenary Year of the Royal Institution, and arrangements are being made with a view to its celebration in a fitting manner. Details will be announced at a later period.

MEETINGS FOR THE WEEK.

Wednesday, 21st.—Microscopical, 7.30.—Exhibition of Binocular Microscopes.

THE CHEMICAL NEWS.

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THE ORIGIN OF THE GASES EVOLVED ON HEATING MINERAL SUBSTANCES, METEORITES, &c.[*]

By MORRIS W. TRAVERS, D.Sc.

THE study of the gases evolved on heating mineral substances has been made the subject of a number of investigations, and the results have formed a basis for speculations as to the origin and history of these substances.

In a paper entitled "The Gases enclosed in Crystalline Rocks and Minerals,"[†] Professor Tilden has suggested a theory to account for the evolution of gases by mineral substances under the influence of heat. He considers that the gases, which are given off on heating certain rocks and minerals, are actually present in those substances in the gaseous state, enclosed in small cavities under high pressure. To account for their presence in these cavities he makes the suggestion, "that the rock crystallised in an atmosphere rich in carbon dioxide and steam, which had been, or were at the time, in contact with some easily oxidisable substance, at a moderately high temperature. Of the substances capable of so acting, carbon, a metal, or the protoxide of a metal, present themselves as most probable."

Beyond the fact that minerals give off gases when heated, there is, except in the case of carbon dioxide, no direct experimental evidence to show that these substances really contain the gases in the free state. In many cases no cavities can be seen in thin sections of the mineral, and as a mineral yields about the same quantity of gas when ground to a fine powder as when it is only broken into small pieces, the cavities must be assumed to be very minute if they exist at all. I do not contend that it is impossible for a rock to contain considerable quantities of gases enclosed in cavities, but I propose to prove experimentally that—at least in some cases where a mineral or rock yields gases other than carbon dioxide on heating—those gases are produced during ignition, by the interaction of its non-gaseous constituents. I shall first consider the formation of carbon monoxide and hydrogen from minerals and rocks which contain as active constituents only water, carbon dioxide, and ferrous oxide.

A glance through the results of the analyses of some such substances, and of the gases evolved by heating them, will show that the quantity of hydrogen and carbon monoxide produced bears a certain relation to the quantity of ferrous oxide and to the quantity of water given off on heating the substance. In the following table the quantities of ferrous oxide and water are expressed in terms of weight *per cent*; the gases in cubic centimetres per grm. of mineral.

Mineral.	Locality.	FeO.	H_2O	H_2.	CO.	CO_2.
Chlorite ..	Zoptan, Moravia	10·6	4·6	2·180	0·494	0·123
Serpentine[‡]	Zermatt	2·7	9·5	0·800	none	none
Gabbro ..	Isle of Skye ..	6·1	1·5	0·490	none	none
Mica	Westchester, Pennsylvania	1·4	0·13	0·08		0·150
Foliated talc[§]	Greiner, Tyrol	0·4	4·5	0·04		0·070
Felspar[‖] ..	Peterhead ..	2·1	1·00	0·214		1·201

The estimation of the ferrous iron was conducted in the following manner:—The sulphuric acid (30 per cent), previously boiled and cooled in a corked flask, was poured into the bottom of a thick-walled glass tube. The mineral was weighed out into a small test-tube with a glass rod sealed to the bottom of it to support it above the sulphuric acid in the large tube during exhaustion. The tube was drawn out at the end as in fig. 1, attached to a Töpler pump by a rubber tube, exhausted, and sealed at the capillary. After heating to 170°—till the mineral was entirely decomposed—the tube was again attached to the pump as in fig. 2, the point of the capillary was broken inside the rubber tube, and the gas contained in it was pumped out and analysed. The tube was afterwards cut open, and the ferrous sulphate was estimated by titration with a solution of potassium permanganate. In the case of the mica it was necessary to use strong sulphuric acid to decompose the mineral.

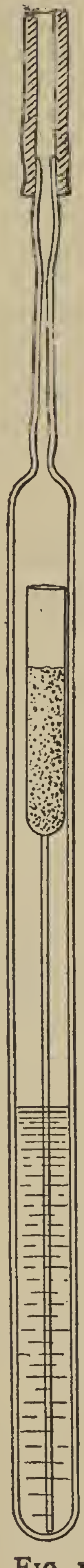

FIG. 1.

FIG. 2.

In general, the gas contained in the sealed tube con-

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[*] A Paper read before the Royal Society, November 24, 1898.

[†] *Roy. Soc. Proc.*, vol. lx, p. 453.

[‡] Analysis by Miss E. Aston, *Quart. Journ. Geol. Soc.*, 1896, lii., p. 456.

[§] The talc lost only 0·06 per cent of water when heated in the hard glass tube; remainder came off at a very bright red heat.

[‖] The felspar contained free iron.

sisted only of carbon dioxide. In the case of the felspar from Peterhead granite, and of certain helium-yielding minerals, the gas also contained hydrogen. I shall deal with these minerals separately.

That the minerals, which on heating give hydrogen and carbon monoxide, give neither of these gases when decomposed by means of dilute sulphuric acid, is almost sufficient evidence to show that the gases are not present in the minerals in a free state, *either occluded* or enclosed in cavities. That the amount of hydrogen and carbon monoxide produced by heating a mineral is, as I have shown, proportional to the amount of ferrous oxide, water, and carbon dioxide present in it, may be taken as evidence that the gases are produced by the interaction of these substances when the mineral is heated, according to the equations—

$$2FeO + H_2O = Fe_2O_3 + H_2$$
$$2FeO + CO_2 = Fe_2O_3 + CO.$$

If this is the case, the mineral, after ignition *in vacuo*, should contain less ferrous oxide than it did originally; the difference between the quantities of ferrous oxide before and after heating should be equivalent to the hydrogen and carbon monoxide evolved; and these may be calculated from the equations written above.

One c.c. of hydrogen or carbon monoxide is equivalent to 0·006428 grm. of ferrous oxide.

In order to prove this experimentally, I selected a chlorite from Zoptan in Moravia. This mineral contained 10·60 per cent of ferrous oxide, 4·79 per cent of water, and consequently gave a considerable quantity of hydrogen on heating. It was also quite free from sulphides, which seriously interfere with the accurate estimation of ferrous oxide.

A weighed quantity, about 10 grms., of the chlorite was heated in a hard glass tube till it ceased to give any gas. The gas was collected and analysed, and the loss of weight of the mineral was determined by weighing the hard glass tube before and after heating.

Analysis of gas expressed in cubic centimetres per gramme:—

CO_2	0·123
CO	0·094
H_2	2·180

Loss of weight on heating, 4·79 per cent.

The mineral was allowed to cool *in vacuo* to prevent the oxidation of the ferrous oxide. The ferrous oxide was estimated in a sample of the mineral before and after heating.

Ferrous oxide in mineral before heating:—

(*a*) 10·62 per cent; (*b*) 10.60 per cent;
mean, 10·61 per cent.

Ferrous oxide in mineral after heating:—

(*a*) 9·70 per cent; (*b*) 9·61 per cent;
mean, 9·65 per cent.

But since the mineral lost weight to the extent of 4·79 per cent on heating, a correction must be applied.

Ferrous oxide in mineral after heating corrected for loss of weight of mineral ..	9·18 per cent
Difference in amount of ferrous oxide present in mineral before and after heating ..	1·43 ,,

The amount of ferrous oxide oxidised to ferric oxide can also be calculated from the quantities of hydrogen and carbon monoxide collected.

2·180 c.c. per grm. of hydrogen is equivalent to	1·401	per cent of	FeO
0·094 c.c. per grm. of carbon monoxide is equivalent to	0·057	,,	,,
Total..	1·458	,,	,,

This number agrees very closely with that already obtained.

The application of this method of investigation is very limited, as it is difficult to obtain minerals which are quite free from sulphides and carbonaceous matter, and which at the same time give on heating a sufficient quantity of carbon monoxide and hydrogen. Other specimens of chlorite gave large quantities of hydrogen on heating, but they were found to contain sulphides.

The minerals and rocks which had been investigated up to this point, had all been of igneous origin. At Professor Bonney's suggestion, I next proceeded to determine whether minerals of aqueous origin, containing ferrous oxide, water, and carbonates, would give hydrogen and carbon monoxide on heating. Professor Bonney kindly obtained for me a specimen of chalk marl, rich in glauconite, from the Cambridge beds.

The glauconite was freed from chalk as far as possible by washing with dilute hydrochloric acid. The residue, seen under the microscope, appeared to consist of foraminiferous casts, with adhering grains of glauconite. The sample taken for the experiment contained 1·33 per cent of ferrous oxide, 15 per cent of water, and 13 7 per cent of calcium phosphate.

Heated in a hard glass tube to a dull red heat for some time, only 5·7 per cent of the water was given off with a considerable quantity of gas, which was found on analysis to have the following composition:—

CO_2	4·518 c.c. per grm.
H_2	3·128 ,,
CO	0·083 ,,
CH_4, &c.	0·204 ,,

On heating to a bright red heat in the flame of a Bunsen burner, the remaining water and more gas was given off:—

CO_2	13·38 c.c. per grm.
H_2, &c...	0·25 ,,

The greater part of the hydrogen and hydrocarbons is probably produced by the breaking down of organic matter in the mineral. This organic matter may be due to infiltration from the surface, but, considering the treatment the mineral had received, it is more probably contained in the formaniniferous casts, the decomposition products of their original occupants.

The presence of manganous oxide in minerals appears also to favour the production of hydrogen and carbon dioxide; indeed, it has long been known, that when moist manganous carbonate is heated, these gases are always produced along with carbon dioxide.

The first reactions which take place when the mineral is heated, may be expressed by the equations:—

$$MnO + H_2O = MnO_2 + H_2.$$
$$MnO + CO_2 = MnO_2 + CO.$$

But it was found that when cerite, a mineral which contains a considerable quantity of manganous carbonate, was heated, the gas contained not only hydrogen, but oxygen, the product of a reaction taking place at a somewhat higher temperature:—

$$3MnO_2 = Mn_3O_4 + O_2.$$

Analysis of the gas obtained by heating finely-powdered cerite gave the following results:—

CO_2	15·0 (about) c.c. per grm.
CO	1·554 ,,
H_2	3·905 ,,
O_2	0·406 ,,

A cobalt ore containing only the higher oxides of manganese gave about 10 c.c. of oxygen per grm. of minerals (*Roy. Soc. Proc.*, lx., p. 444).

Yttrotantalite, samarskite, &c., containing lower oxides of uranium, also give small quantities of hydrogen when heated. The hydrogen may be produced according to the equation—

$$3UO_2 + 2H_2O = U_3O_8 + 2H_2.$$

The quantity of hydrogen is not, however, very large.

Minerals containing sulphides usually give a mixture of hydrogen, sulphuretted hydrogen, and sulphur vapour when heated. The quantity of gas is often very large, but the reaction is too complicated for direct investigation. It is probable that the sulphides react with water, forming sulphuretted hydrogen, which at the temperature of the reaction is decomposed into sulphur and hydrogen.

It is known that certain crystalline minerals contain liquid hydrocarbons enclosed in cavities. It is also possible that the methane, and other hydrocarbons sometimes present in the gases obtained by heating mineral substances, may be produced by the destructive distillation of bituminous matter infiltrated into it, or from vegetable matter, particularly if the specimen has been long exposed on the surface.

Nitrogen I have only rarely obtained by heating minerals. Malacone (*Roy. Soc. Proc.*, 1897, vol. lx., p. 444) yields it in larger quantity, compared with the total quantity of gas evolved, than any other mineral which I have examined, but even in that particular case only a very small quantity of the gas is obtained. It is possible that a finely powdered mineral may on standing condense air on its surface. Dr. G. McGowan tells me that when a sample of china clay was heated in a current of hydrogen a small quantity of ammonia was given off. Certain bituminous shales, in which the organic matter is certainly of animal origin, are known to contain large quantities of ammonium salts; the gases evolved under the influence of heat would certainly contain nitrogen. Nitrogen and its oxides might also be the product of the interaction at a high temperature of nitrates infiltrated into the rock and silica. That Davy obtained nitrogen from quartz is highly improbable. It is more likely that the gas was introduced accidentally in the course of the experiment.

I stated earlier in this paper that the felspar from Peterhead granite exhibited certain peculiarities, and that I should describe it separately. The granite consisted of very large crystals of quartz and felspar, with a comparatively small quantity of mica of a dark colour. On heating, a mixture of carbon dioxide, carbon monoxide, and hydrogen was driven off.

In order to ascertain whether these gases were derived from each of the minerals, or whether any particular one gave more gas on heating than the others, I crushed a large quantity of the granite in an iron mortar and picked out the constituents, separating them from one another as far as possible. The mica was easily obtained quite pure, but the quartz and felspar could not, without very great trouble, be separated from one another; in fact, the felspar always contained a considerable quantity of the latter mineral.

By heating weighed quantities of the component minerals to red heat in hard glass tubes, and collecting and analysing the gases, the following results were obtained. The results are expressed in cubic centimetres of gas per grm. of mineral:—

	Quartz.	Mica.	Felspar.
Carbon dioxide	0·225	none	0·172
Carbon monoxide ..	0·074	none	0·059
Hydrogen		0·164	0·218

These results show that the mica and felspar are responsible for nearly the whole of the hydrogen, while the greater part of the carbon dioxide is derived from the quartz. The carbon dioxide is probably present in cavities in the quartz, but if the hydrogen were also present in cavities, one would expect that it would be also obtained in greatest quantity from the quartz, the only mineral of the three which has no cleavage; one would not certainly expect to obtain it from the mica.

As the felspar gave off gas in the cold when treated with dilute sulphuric acid, a weighed quantity of the mineral was placed in a thick-walled tube, with a second tube containing 50 per cent sulphuric acid. The tube was drawn to a point, exhausted, and sealed in the manner already described. After heating for twenty-four hours to 170° the gas was pumped out and analysed, and the ferrous sulphate in the solution was determined.

The following results were obtained from two samples of felspar from different parts of the same block of granite. The quantities of gas are expressed in cubic centimetres per grm.:—

Ferrous oxide in solution	(*a*) 4·02 p.c.	(*b*) 2·05 p.c.
Hydrogen with trace of hydrocarbon	3·50 ,,	1·99 ,,
Carbon dioxide	0·20 ,,	0·90 ,,

From these results I was led to suppose that the felspar contained both free iron and ferrous oxide, since, if we calculate the amount of iron which would be equivalent to the hydrogen evolved, we find that expressed in terms of ferrous oxide:—

3·50 c.c. of hydrogen per grm. = 2·25 per cent of ferrous oxide.

1·99 c.c. of hydrogen per grm. = 1·23 per cent of ferrous oxide.

Quantities which are considerably less than the quantity of ferrous oxide found by titration. On the other hand, it is possible that some of the hydrogen is taken up by the ferric compounds present, lessening the yield of hydrogen, and increasing the quantity of ferrous sulphate in the solution.

There is, unfortunately, no accurate method of estimating the free iron in minerals. The copper method apparently fails in the presence of hydrated ferric oxide, on account of the secondary reactions which take place between that compound and copper sulphate, and subsequently between the ferric sulphate and precipitated copper.

In order to prove that a considerable amount of free iron was present in the felspar, two weighed quantities of felspar from the same sample were heated with 50 per cent sulphuric acid and 96 per cent acid respectively. The gases were subsequently pumped out of the tubes and analysed, and the ferrous sulphate was estimated in the liquid.

The following results were obtained:—

(*a*) With strong sulphuric acid, carbon dioxide and sulphur dioxide ..	1·26	c.c. per grm.
Hydrogen and trace of hydrocarbons	0·49	,,
Total	1·75	,,
Ferrous oxide	2·07	per cent.
(*b*) With 50 per cent sulphuric acid, carbon dioxide	0·23	,,
Hydrogen and trace of hydrocarbons	1·64	,,
Total	1·87	,,
Ferrous oxide	2·26	per cent.

These figures indicate that the sulphur dioxide and hydrogen produced by the action of the strong acid is just equivalent to the hydrogen produced by the dilute acid, indicating that the felspar contains metallic iron, which is probably the source of the whole of the hydrogen evolved when the mineral is treated with acid. The hydrogen and carbon monoxide given off on heating the felspar are produced by the action of water and carbon dioxide on ferrous oxide and metallic iron present in the mineral.

Both the gas obtained by heating the felspar and gases obtained from the sealed tube experiments contained traces of hydrocarbon. This may be accounted for on the assumption that the free iron in the felspar contains a small quantity of carbide.

(To be continued).

NOTES UPON THE SYNTHESIS OF ETHYL ALCOHOL.

By FRANK WOOD.

According to the text-books, with their proverbial self-assurance, it is quite an easy matter to synthesise ethyl alcohol. We are told that all that is necessary is to convert acetylene (made by sparking across two carbon points in an atmosphere of hydrogen) into ethylene by means of nascent hydrogen, or by passing a mixture of acetylene and hydrogen through a red-hot tube; the ethylene so produced is then passed into hot concentrated sulphuric acid, and the ethyl sulphuric acid thus formed on distillation with water yields ethyl alcohol.

I have performed the following experiments in order to synthesise alcohol; assuming, however, that acetylene can be obtained synthetically by the electrical sparking process, I made my acetylene by other methods.

1. Acetylene, generated from calcium carbide by the action of water, was then mixed with hydrogen in a large tube filled with $CaCl_2$, and the mixed gases were then passed through 18 inches of red-hot combustion tubing containing layers of red-hot woolly asbestos; the effluent gases were received in pure sulphuric acid in potash bulbs, in one case cold and in another heated to 170° C.; in both instances the acid became very dark brown, but neither of the acids, after large dilution with water and distillation, yielded even a trace of ethyl alcohol. The asbestos after the experiment was found to contain a considerable quantity of brownish-black carbonaceous dust, showing that the acetylene and hydrogen had reacted somewhat as follows:—

$$C_2H_2 + H_2 = C_2 + 2H_2.$$

As I was not seeking to prepare carbon or hydrogen, this could scarcely be considered a satisfactory result.

2. Calcium carbide and zinc dust were intimately mixed and put into a suitable generator, dilute sulphuric acid was gradually allowed to enter automatically, and the gases evolved were dried and passed through strong H_2SO_4 heated to 170° C. As in the previous case, the acid became a very dark brown colour, and on dilution and distillation gave no trace of alcohol; it yielded instead rather a fragrant odour of cedar-wood oil, which, however, was not the object of my quest.

3. Text-books strongly recommend copper acetylide, so I next tried to produce ethyl alcohol by its use. This substance in the wet state was ground up to a paste with zinc dust, and the gases evolved by the addition of dilute sulphuric acid were dried and passed through a red-hot tube into pure H_2SO_4 at 160 to 170° C. The usual results—that is, the enormous production of black carbonaceous substance and a dirty brown non-ethylated sulphuric acid—were obtained.

4. Relying upon the concise dogmatism of the text-books which state that copper acetylide and zinc dust, when treated with ammonia, give ethylene, I tried an experiment on similar lines to the foregoing, only with the use of ammonia instead of dilute H_2SO_4, and with the abolition of the red-hot tube. In the cold the ammonia produced a considerable supply of gas, which I fear could only be acetylene, as under the same conditions zinc dust gave no evolution of hydrogen. Of course this result was also negative as far as the production of alcohol was concerned, so—whether I used a high or a low temperature, or acetylene with or without nascent hydrogen—no alcohol was obtained in any case.

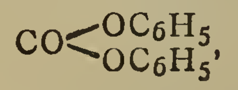
I have consulted Beilstein, the *Berichte*, the *Journal of the Chemical Society*, and a number of chemical journals and text-books, but so far have not been able to meet with an article by the original person whose statements have since inspired a whole succession of text-book writers; possibly some of your readers may be able to throw some light upon a subject which to me appears inscrutable.

ON A

GENERAL METHOD FOR THE PREPARATION OF MIXED CARBONIC ETHERS OF THE FATTY AND AROMATIC SERIES.

By P. CAZENEUVE and A. MOREL.

By causing chlorocarbonate of ethyl to react on the sodic or potassic phenols, Fatianow (*Jahresb.*, 1864, p. 477), Richter (*Journ. f. Prakt. Chem.*, Series 2, xxvii., pp. 503 and 511), and Bender (*Deutsch. Chem. Gesellsch.*, 1880, p. 696), obtained mixed carbonic ethers of ethyl and various phenols. We have succeeded in preparing these mixed carbonates in a different and more practical manner, *by heating neutral phenolic carbonates in the presence of certain organic bases, in different alcohols.* Carbonate of phenyl in particular—



$$CO{<}\begin{matrix}OC_6H_5\\OC_6H_5\end{matrix},$$

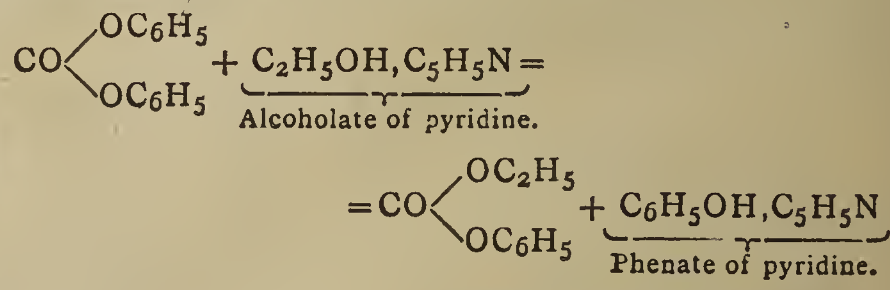
heated with urea in various homologous alcohols of the fatty series, gives mixed carbonates of phenyl and these different alcohols. We have thus been able to obtain good returns of the mixed phenylic carbonic ethers; of methylic, ethylic, propylic, secondary propylic, isobutylic, and isoamylic alcohols, and even the carbonate of phenyl-allyl.

With the exception of phenyl ethyl, these ethers were hitherto unknown. Some of these ethers were obtained in a very pure state, and gave good results on analysis. Some others, in proportion as they rise in the series of alcohols, are more difficult to purify, on account of the formation of allophanates and urethanes, which pass over even when distilled *in vacuo*.

Other bases act in the same manner as urea, without giving rise to these inconvenient impurities. In this way aniline, sulphanilate of soda, dimethylaniline, pyridine, quinolein, and dimethyl piperazine when heated with carbonate of phenyl to boiling point for several hours in the presence of a large excess of ethylic alcohol, give carbonate of ethyl and phenyl.

Turning to the other carbonates of phenol, carbonates of gaïacol, thymol, cresol, &c., with various alcohols, we obtain the corresponding mixed carbonates.

The intervention of bases is necessary. The phenolic carbonates heated alone in the alcohols remain unchanged. Carbonate of phenyl, heated to boiling-point for several days in alcohol at 93°, gives, however, a little mixed carbonate; but the reaction is very slow. The bases stimulate the reaction, and even cause it in the cases of the numerous phenolic carbonates with which we have experimented. Without doubt the action of the bases is to form alcoholates which cause the double decomposition according to the following equation:—



$$CO{<}\begin{matrix}OC_6H_5\\OC_6H_5\end{matrix} + \underbrace{C_2H_5OH,C_5H_5N}_{\text{Alcoholate of pyridine.}} =$$

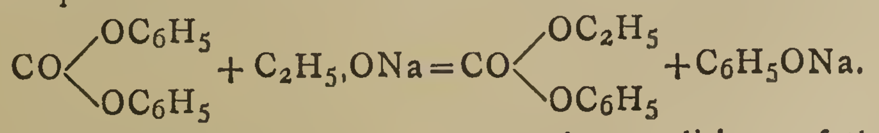
$$= CO{<}\begin{matrix}OC_2H_5\\OC_6H_5\end{matrix} + \underbrace{C_6H_5OH,C_5H_5N}_{\text{Phenate of pyridine.}}$$

The affinity of the base for phenol hastens the decomposition.

Further, the acid-alcohol character of the carbonic acid is not strange to this formation of mixed carbonate; the decomposition takes place preferably on the acid group of the carbonic acid. The alcohol group of the carbonic acid, etherified by phenol, is, according to the regular rule, less saponifiable and much more stable.

As a further proof of the mechanism we have applied to explain the formation of these mixed carbonic ethers, we would draw attention to the very characteristic action of the soda-alcoholates.

The reaction takes place rapidly, and in most cases in the cold. By adding 1 molecule of ethylate of sodium dissolved in an excess of absolute alcohol, to 1 molecule of carbonate of phenyl dissolved in a mixture of alcohol and ether, we obtain 60 per cent of the mixed carbonate. Care must be taken to moderate the reaction by cooling, otherwise a double carbonate of ethyl will be produced. The reaction takes place according to the following general equation:—



$$CO\begin{matrix}\diagup OC_6H_5\\ \diagdown OC_6H_5\end{matrix} + C_2H_5{,}ONa = CO\begin{matrix}\diagup OC_2H_5\\ \diagdown OC_6H_5\end{matrix} + C_6H_5ONa.$$

It is necessary only to arrange the conditions of the reaction for each particular case.

Numerous mixed carbonic ethers from different phenols and alcohols have been thus prepared, and will be shortly described. Sometimes, however, we get a double alcoholic carbonate.

To sum up, this general method is the easiest and most profitable for preparing the mixed carbonic ethers of the fatty and the aromatic series, and consists of making the sodic or potassic alcohol derivatives react on the carbonates of the phenols, or, what is better in certain cases, using alcoholic solutions of organic bases.—*Journ. de Pharm. et de Chim.*, Series 6, vol. ix., No. 2.

THE ESTIMATION OF PERCHLORATE IN CHILI SALTPETRE.

By O. FOERSTER.

The usual methods for the estimation of the chlorates and perchlorates in saltpetre—methods based on reduction by calcination for two hours at a dull red heat—do not give very exact results. The cause of error rests principally in the volatility of the alkaline chlorides, and partly in the loss of chlorine by the decomposition of these latter. It may also be due to the insufficient reduction of the oxygenated compounds of chlorine. Further, melted saltpetre has an inconvenient tendency to creep over the edge of the crucible, which will occasion losses. To guard against this loss it is necessary to use very large crucibles, and it is not easy to heat them in a uniform manner.

The following process, which is very simple and allows of the rapid and complete reduction of the chlorates and perchlorates, is free from all the objections just mentioned:—10 grms. of the saltpetre to be analysed are mixed with 10 grms. of anhydrous carbonate of soda free from chlorine, and the mixture heated over a strong flame in a covered platinum crucible, or in a large porcelain crucible, until it becomes liquid and no longer gives off gas bubbles; this will not take more than ten minutes. The melted mass does not adhere strongly to the sides, and after cooling is completely dissolved in excess of nitric acid. In the solution thus obtained the total chlorine is estimated in the usual manner. This method leaves nothing to be desired in the way of exactitude.

In a mixture of 10 grms. of nitrate of soda free from chlorine and 10 grms. of anhydrous perchlorate of potash, treated as described above, the following results were found on titrating with sulphocyanide of potassium, by Volhardt's method:—

I. 0·49990 $KClO_4$ = 99·88 per cent of the quantity used.
II. 0·50004 ,, = 100·01 ,, ,,
III. 0·49921 ,, = 99·84 ,, ,,

The following experiment shows that there is no loss of chlorine caused by the decomposition of chlorides and chlorates; in a mixture of 10 grms. of $NaNO_3$ and—

0·1012 grm. NaCl (= 0·06132 grm. of Cl),
0·1012 grm. $KClO_3$ (= 0·02927 grm. of Cl),
0·1006 grm. $KClO_4$ (= 0·02574 grm. of Cl),

the mixture therefore contained a total of 0·11633 grm. of chlorine, and 0·11627 grm. Cl was found,—that is to say, 99·95 per cent of the quantity used.—*Chemiker Zeitung*, 1898, p. 357.

THE SOLUTION OF SOLIDS AND LIQUIDS IN GASES.

By P. VILLARD.

(Concluded from p. 298).

V. *Critical Phenomena.*

If chloride of ethyl, for example, is put in the presence of compressed formene, we notice that at 200 atmospheres and 17° the surface of the liquid loses its distinctness and becomes transformed into a zone of transition several millimetres thick. On agitation the two fluids form a homogeneous mixture. This phenomenon is in every way similar to that observed when we heat a liquid in a closed vessel up to its critical temperature. We have to deal with a true critical point, as already noticed by M. Cailletet in the case of liquid carbonic acid and air.

The pressure at which the surface disappears varies with the temperature. We can thus observe the phenomenon in two ways: 1st, by raising the temperature and keeping the pressure constant; 2nd, by increasing the pressure while maintaining a constant temperature. For any given gas and liquid there will thus be an infinity of critical points, each corresponding to a definite temperature and pressure.

The explanation of these phenomena is very simple; the solubility of the liquid in the gas increases when the temperature or the pressure is raised. At any given temperature, if the pressure is sufficiently great, formene saturated with chloride of ethyl, for example, will have the same composition as chloride of ethyl saturated with formene, and the two fluids will mix: this is what takes place at 17° under a pressure of 200 atmospheres; with sulphide of carbon and formene, at the same temperature, it is necessary to have a pressure of 550 atmospheres.

The phenomena observed in the neighbourhood of this critical point are exactly similar to those observed in ordinary Natterer tubes; the cause is, however, different, and does not consist, as in these latter, in a want of thermic equilibrium; the results are, in fact, the same when the pressure only is varied.

The formation at the critical point of a zone of transition arises from the fact that the reciprocal saturation of the two fluids can only take place at their surface of separation, unless the diffusion is aided by agitation. It is thus only in the immediate neighbourhood of the surface that the liquid and the gas can become of the same density; it is no longer so at a little distance away: this causes a continuous variation of the density, and of the index of refraction along the whole length of the tube. The analogy with liquefied gases is again met with in the appearance caused by condensation. If, for example, the pressure is lowered in a tube containing two fluids previously brought to the critical pressure, a simultaneous boiling and rain takes place; the resemblance with what takes place near the critical temperature in a Natterer tube which is cooled is complete. This phenomenon is easily explained; by releasing the pressure the liquid gives up a part of the dissolved gas, and *vice versâ*.

VI. *Applications.*

The use of gaseous solvents furnishes a new solution of the problem of the distillation of bodies decomposed by heat. As a rule we have recourse to a vacuum when dealing with bodies of this nature; their boiling-point can then be sufficiently reduced that, as a rule, decomposition need not be feared; but this process cannot evidently be applied to bodies so little volatile as stearic acid for instance. Another inconvenience of this method is, that at a low temperature the vapour tension is often very much reduced. The vaporisation, it is true, is very active, but each litre of vapour represents only an insignificant quantity of material.

There would be a very great advantage in substituting for distillation, solution in a suitable gaseous medium. This is equivalent to considerably augmenting the volatility of the substance in question. By reducing the pressure of the atmosphere the whole of the substance dissolved would be deposited, the dissolving power of the gas becoming practically *nil*. This is a very great advantage over liquid solvents. The most volatile bodies being at the same time the most soluble, an operation of this character would give results analogous to those obtained by distillation, but it would be much more rapid, and could further be applied to bodies such as wax or paraffin, or even to explosive substances. The apparatus required would only be a reservoir of compressed gas and a few tubes of thick glass or metal furnished with taps.

This method of distillation is not only applicable to laboratory experiments. Compressed gas is now an article of commerce, and apparatus capable of withstanding pressures of several hundreds of atmospheres is easily obtained. There should, therefore, be no difficulty in adding compressed gas to the list of solvents employed in industrial chemistry.—*Revue Générale des Sciences*, No. 21, Nov. 15, 1898.

ELECTROLYTIC DETERMINATION OF TIN IN TIN ORES.*

By E. D. CAMPBELL and E. C. CHAMPION.

In the methods at present in use for the determination of tin in tin ores, the decomposition is effected by fusion with sodium carbonate and sulphur, in order to form sodium sulphostannate, from which the tin is obtained either by precipitation as sulphide with subsequent ignition to the oxide, or by electrolytic deposition from the ammonium sulphide or oxalate solution. Some of the objections to the Rose method of precipitation as stannic sulphide and subsequent weighing as stannic oxide are the difficulties of washing the sulphide free from sodium salts, the ignition to stannic oxide without loss of stannic sulphide, and the contamination of stannic oxide with silica.

Electrolytic deposition of tin from the ammonium sulphide solution does not seem to give entirely satisfactory results, for although the tin may be completely precipitated, it is very difficult to obtain complete deposition without at the same time precipitating some sulphur. On the other hand, under proper conditions, tin may be very satisfactorily deposited electrolytically from the double oxalate solution; and in the method herewith proposed, the principal modification is in the method of converting the tin from the sulphostannate into the double oxalate. In the method as given by Classen for the conversion of sodium sulphostannate into the double ammonium oxalate, the solution of the sulphostannate is first acidified with sulphuric acid, and the tin then oxidised to metastannic acid by means of hydrogen peroxide. The metastannic acid so formed has to be filtered, washed, and dissolved by means of ammonium acid oxalate and oxalic acid, in order to convert it into the double oxalate ready for electrolysis. It was in order to avoid any necessity of precipitating the tin and filtering it out, after it had been once obtained in solution as sodium sulphostannate, that the method given below was perfected. The method in detail, which has given us very satisfactory results on ores tested, is as follows:—

Mix one grm. of finely ground ore intimately with five to six grms. of a fusing mixture made up of equal weights of dry sodium carbonate and sulphur. Place the ore so mixed in a covered porcelain crucible, which in turn should be in a larger covered porcelain crucible. This arrangement of double crucibles will prevent oxidation of stannic sulphide during the ignition. Place the crucible upon a triangle, and cover with a large Hessian or clay crucible, from which the bottom has been removed, in such a way that the heat from the burner used in the ignition will be kept in, so that the whole of the porcelain crucible will be evenly heated. Raise the temperature of the porcelain crucibles by means of a good burner, such as the Detroit or Fletcher style, to a full red heat, and maintain the temperature for one hour. After allowing it to cool, place the inner crucible in a beaker or casserole, and dissolve out the sodium sulphostannate by heating with 40 or 50 c.c. of water. After complete disintegration of the fused mass, remove the porcelain crucible from the solution, and filter out the insoluble oxides and sulphides from the solution, which will contain almost all the tin as sodium sulphostannate. Wash the insoluble residue with hot water. This insoluble residue will usually carry a small amount of tin, and must therefore be ignited in the crucible in which the fusion was performed, and after ignition be re-fused, as in the first case, with fresh sodium carbonate and sulphur. After fusing the insoluble residue from the first fusion and dissolving out the tin, unite the solutions of sodium sulphostannate. Add to the united solutions of sodium sulphostannate hydrochloric acid, until the solution is slightly acid and the tin has been precipitated as stannic sulphide. Boil down rapidly, until the excess of hydrogen sulphide has been boiled off and the bulk of the solution has been reduced to 75 or 80 c.c. Add to the hot solution 10 c.c. of hydrochloric acid (sp. gr. 1.20). Then stir in, a little at a time, sodium peroxide, until the stannic sulphide has been completely oxidised to stannic chloride, and the solution has become clear, except for a little sulphur which collects easily on boiling for two or three minutes, and can be easily removed by filtering.

The oxidation of stannic sulphide to stannic chloride is very easily effected, requiring usually from 2 to 3 grms. of sodium peroxide. After oxidising the stannic sulphide to stannic chloride, boil two or three minutes until the separated sulphur is collected, then filter into a large platinum dish, and wash thoroughly with a little hot water. Add to the solution ammonia until a slight permanent precipitate is obtained, then 50 c.c. of a 10 per cent solution of acid ammonium oxalate. This will give a clear solution from which the tin is easily deposited.

Electrolyse over night with a current $N. D._{100} = 0{\cdot}10$ ampere, with an electromotive force of 4 volts. This current can be obtained from two storage cells using suitable resistance. In the morning the tin will be found to be completely precipitated as a pure white, firmly adherent metal upon the platinum dish. When 8 volts E.M.F. were used the deposit was found to be more strongly crystalline and less firmly adherent than when lower voltage was employed. When the tin is completely deposited, disconnect and wash the tin first with water, then with alcohol. Drain off the latter as completely as possible, and dry between 80° and 90° C. If the deposited tin is found to have small crystals of ammonium oxalate adhering to it, they may be easily removed by washing with a little warm water before the final washing with alcohol. After weighing the platinum dish containing the precipitated tin, the latter is dissolved off by heating with a little hydrochloric acid, and the weight of the platinum dish obtained after washing and drying as before.

In electrolytic determination of metal where they are deposited in platinum dishes, the results will be found to be much more satisfactory if duplicate determinations are made in platinum dishes of practically the same size, and the dishes are washed, dried, cooled, and weighed under

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[*] Contribution from the Laboratory of Analytical Chemistry, University of Michigan. From the *Journal of the American Chemical Society*, xx., No 9, September, 1898.

the same conditions, each dish serving as a counterpoise for the other. By using dishes in this way, variations of weight due to atmospheric changes may be reduced to a minimum, and the results made more accurate than when a dish is weighed alone.

LUBRICANTS FOR GLASS STOP-COCKS.

By FRANCIS C. PHILLIPS.

The success of modern chemical research work depends frequently upon the maintenance in position for considerable periods of complex forms of apparatus in which glass stop-cocks play an important part, and the failure or breakage of a stop-cock often proves to be the cause of serious loss of time or material. The efficiency of a stop-cock is, however, quite as much dependent upon the lubricant used for its protection as upon the skilful workmanship of the glass-blower in its manufacture.

It has been the common practice to employ an animal fat or a mixture of such fats for lubricating the stop-cock plugs of apparatus of all kinds and for work of every description, although it is a fact of experience that such lubricants are often a source of inconvenience and even danger to the apparatus.

A stop-cock lubricant should, besides overcoming friction, satisfy the following requirements:—

1. It should adhere to the glass, and should not be loosened by water.
2. It should be little affected by changes of temperature.
3. It should not be saponified by alkali.
4. It should be sufficiently transparent or translucent to render visible any clogging of the hole in the stop-cock plug while in use, and to show whether air spaces occur between the plug and the walls of the stop-cock.

Ordinary fats are so easily saponified and adhere so feebly to glass that they are seldom suited to the purpose. Pure rubber heated to a temperature sufficient to render it permanently viscid has advantages over fats, but its adhesiveness is lessened by moisture, and it is completely removed by alkali.

Schmitz (*Ztschr. Anal. Chem.*, 1884, 516) recommends for glass stop-cocks the use of gutta percha dissolved in a high-boiling mineral oil. This mixture, although not saponifiable, does not adhere well to glass. If thinned down sufficiently with oil, its lubricating qualities suffer, while the gutta percha tends to become granular if the mixture is made thicker.

Vaseline, which is sometimes recommended for use alone, does not adhere to the glass, and does not overcome friction.

With a view to producing a lubricant better adapted to use on glass stop-cocks, a series of experiments has been tried. Various mixtures of softened rubber with other substances were tested. On mixing together

Pure rubber	70 parts.
Spermaceti	25 ,,
Vaseline	5 ,,

a mass is obtained which lubricates well, is translucent, adheres to the glass, and is not saponifiable. The vaseline was added to the mixture to increase its softness. The materials were thoroughly mixed while hot, the rubber being melted first, and the others stirred in. It is well to use a little more vaseline in winter than summer.

Another preparation, which gave still better results, was made by mixing

Pure rubber	70 parts.
Yellow unbleached beeswax ..	30 ,,

The rubber should be pure and fresh. Old rubber, or scraps of worn out tubing, whether black or red, will not answer as well, and may cause the mixture to become more or less granular and opaque when used in the stop-cocks. The rubber is best heated in a covered vessel until thoroughly melted, and then the wax should be added. The hot mixture is well stirred. No vaseline is needed. This lubricant is very serviceable, protects stop-cocks from sticking, even when used for concentrated solutions of caustic alkalies, and is quite translucent in thin layers. Care should be used not to scorch the mixture in its preparation. Strong alkalies tend in time to loosen and emulsify all lubricants, and the stop-cocks should occasionally be cleaned and re-coated.

It has been attempted to increase the adhesiveness of such lubricants by the addition of small quantities of balsam of fir and other strongly adhesive substances, but difficulty was found from the tendency to cause sticking of the stop cock plug. The rubber mixtures should not be exposed to the air longer than is necessary during the heating, and they should be preserved in closed bottles.

Various mixtures of gutta percha with wax and with oils were tried, but the gutta percha tends to cause granulation and diminishes adhesiveness. The mixtures above recommended may be readily removed from parts of glass apparatus, which are difficult of access for cleaning, by the use of a little concentrated nitric acid, which quickly attacks and loosens it so that it may be washed out by water.

No lubricant is fit for use unless it renders the stop-cock nearly or quite translucent, so as to show whether or not the plug is coated over its entire length.

A thick rubber and wax mixture is especially suited for well-ground glass stop-cocks upon gas vessels which are to be exhausted, and which have therefore to sustain the full pressure of the atmosphere. Such mixtures have been in use for stop cocks of ordinary burettes in volumetric work during about two years, and have given satisfactory results in every way.—*Journal of the American Chemical Society*, xx., No. 9.

THE ALKALINE REACTION OF SOME NATURAL SILICATES.*

By F. W. CLARKE.

That pure water exerts a distinct solvent action upon many natural silicates has long been known. As far back as 1848 the Rogers Brothers published a series of observations upon this subject, (*Am. Journ. Sci.*, vol. v., No. 2, 401), and showed that some species of minerals would give an alkaline reaction to test paper. They did not, however, give details concerning the individual minerals thus investigated. The more recent researches of Daubrée and of Cossa are well known.

By the use of phenolphthalein as an indicator the alkalinity of many silicates can be demonstrated with the utmost ease, and the experiments described below serve to bring out very clearly the relative decomposability of certain minerals and rocks by pure water. The method adopted was as follows: A series of glass-stoppered bottles was placed against a white background. In each bottle half a grm. of finely pulverised mineral was put, and then 50 c.c. of distilled water, containing a very little alcoholic phonolphthalein, was added. As the indicator was mixed, once for all, with the total amonnt of water taken for the entire series, the 22 samples examined were treated exactly alike. Two of the bottles were filled with the water and indicator in blank, in order that possible action upon the glass itself might be detected if it occurred. The two blanks, however, remained colourless

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* Read at the Boston meeting of the American Chemical Society, August, 1898. From the *Journal of the American Chemical Society*, vol. xx., No. 10.

during the two weeks through which the experiments lasted. The results obtained were as follows:—

Muscovite.—A doubtful trace of colouration, which soon disappeared.

Lepidolite.—Like muscovite.

Phlogopite.—The peculiar non-fluoriferous variety from Edwards, N.Y. Gave a very distinct, permanent, pink colouration.

Orthoclase.—A trace of colouration which increased for a few days and then faded.

Oligoclase.—The transparent variety from Bakersville, N.C. Distinct and permanent, but pale colouration.

Albite.—From Amelia County, Va. Gave a good, permanent, alkaline reaction.

Leucite.—A slight reaction at first, which faded in a few days.

Nephelite.—The elæolite from Litchfield, Maine. Good colouration, but partly fading in time.

Cancrinite.—Litchfield, Maine. Gives a deep rose colouration, which is permanent.

Sodalite.—From Canada. A deep, permanent rose colour.

Spodumene.—The transparent, yellow variety from Brazil. A good reaction, but gradually fading.

Scapolite.—The wernerite from St. Lawrence County, N.Y. Gave a faint, evanescent trace of colouration.

Laumontite.—A doubtful trace of colouration.

Stilbite.—Faint, evanescent colouration.

Chabazite.—Like stilbite.

Heulandite.—Slight reaction, but distinct.

Thomsonite.—Variety lintonite. A fairly strong reaction, fading in time,

Analcite.—Good alkaline reaction.

Natrolite.—From Bohemia. Strong colouration, permanent.

Pectolite.—From Bergen Hill. Gave a very deep rose colour.

Apophyllite.—From Bergen Hill. A very deep rose colour.

In nearly every case the reaction was obtained at once, showing a more rapid action of water upon the silicate than had been anticipated. In some instances fading is noted. This is doubtless due, in general, to the action of light; but in certain cases the coloured solution separated into two layers, the colour being wholly in the lower. Here the colour was really held as a coating upon the fine solid particles, and as they subsided the appearance of stratification was produced. Towards the end of the experiments the mineral aegirite was added to the series. This also gave a strong alkaline reaction and a fairly deep rose colour.

A neat method of demonstrating the reactions described above is the following:—Place a little of the mineral to be tested in a watch-glass upon a sheet of white paper. Add a drop of alcoholic phenolphthalein solution, and then a few drops of pure water; in most cases the reaction is given instantaneously. Orothoclase gave no colouration, leucite a trace, and scapolite a trace; albite, nephelite, and phlogopite furnished distinct reactions. Under the same circumstances thomsonite, aegirite, natrolite, cancrinite, sodalite, pectolite, and apophyllite gave immediately a deep rich rose colour. The strongest alkaline reactions seemed to be given by pectolite and apophyllite.

In general, the order of intensity of the colour produced was what might have been expected. Among the micas, muscovite and lepidolite showed little or no solubility, while phlogopite was distinctly attacked. In nature the magnesian micas are far more easily alterable than muscovite, a fact which is reiterated by these experiments. Again, orthoclase was slightly dissolved, albite much more so, and oligoclase gave a reaction between the two; that is, more than the one, less than the other. In other words, the plagioclase felspars alter more easily than orthoclase, as is apparent in the study of the rocks themselves.

In order to bring out the latter point more clearly, a series of rocks which had been analysed in the laboratory of the U.S. Geological Survey, was placed in a row of bottles, and treated just as the mineral species had been, with water and phenolphthalein. A granite and an amphibole gabbro gave no alkaline reaction. A rhyolite, trachyte, leucite basalt, felspar basalt, and diorite gave faint traces of colour. Granitite, gneiss, phonolite, diabase, and camptonite yielded distinct alkaline colourations.

In all of these instances the production of colour is doubtless due to the solution from the mineral or rock of alkaline silicates. The noteworthy point is the quickness with which the reaction can be obtained. With minerals like cancrinite, sodalite, natrolite, pectolite, and apophyllite the reaction is striking enough to be used as a lecture-table experiment.

THE GASES OF THE ATMOSPHERE.

Berlin, *Dec.* 19.

Professor William Ramsay this evening delivered a lecture by special invitation to the members of the Berlin Chemical Society in the Chemisches Institut. Professor Liebermann presided and welcomed his distinguished English colleague in words conveying the most cordial recognition of his achievements. There was a crowded audience, among whom were Professor Virchow, Professor Liebreich, Professor von Bezold, Professor Warburgh, Professor Fischer, and, in fact, every chemist of eminence in Berlin.

Professor Ramsay had chosen for his subject "The New Gases and their Relations to the Periodic Law." He gave a most interesting account of the various properties of helion, argon, metargon, neon, and xenon, and illustrated his more recent investigations by limelight views of the appliances of his laboratory and by the spectra of the various gases, most of those present following his explanations with the aid of pocket spectroscopes. The lecture, which was very fluently delivered in German, paid warm tribute to the work of Lord Rayleigh and to the assistance rendered to Professor Ramsay in the course of his experiments by Dr. Travers and others. At its close, amid loud cheers, Professor Liebermann thanked the distinguished lecturer for having devoted a portion of his vacation to the instruction of his Berlin colleagues and admirers, and described him as having by his indomitable energy and perseverance united the realms of physics and of chemistry.

Berlin, *Dec.* 20.

The Emperor and Empress this afternoon were present at a lecture and demonstration by Professor Ramsay dealing with the recently discovered gases. The lecture was delivered at the Chemisches Institut in Berlin, by special desire of her Majesty, and was, therefore, of a semi-private character. Their Majesties, accompanied by the British Ambassador, Sir Frank Lascelles, whom the Emperor had graciously invited to be present, occupied chairs in front of the auditorium. Professor Ramsay spoke in English for about half-an-hour, and illustrated his account of the new gases by limelight views and by Geissler tubes for exhibiting the spectral analysis of the gases. At the close of the lecture, the Emperor and Empress conversed for some time with Professor Ramsay.

Professor Ramsay was last night the guest of the Berlin Chemical Society at supper in the Savoy Hotel. To-morrow he will comply with a request which has been made to him to deliver a lecture in the Urania, the Berlin popular institute of astronomy and other sciences.—*The Times*, December 20 and 21.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 17th, 1898.

Professor Dewar, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. William Harcourt Branscombe, Verona, Eastbourne; Harry Estcourt Estcourt, Hayesleigh, Old Trafford, Manchester; George Cecil Fry, 1, Edinburgh Terrace, Newbury, Berks; John Golding, 1, Balmoral Road, Nottingham; Henry Winstone Harper, M.D., Austin, Texas, U.S.A.; James Hembrough, 159, Hotwell Road, Clifton, Bristol; Alfred Lucas, Maison Hussein Pasha, Cairo, Egypt; Samuel Montagu Martin, Westwood, Princetown Road, Bangor, co. Down; James Henry Pizey, 9, Lady Somerset Road, Highgate Road, N.W.; Robert Coleman Price, Blacksburg, Virginia, U.S.A.; Frederick Soddy, Merton College, Oxford; Louis Heathcote Walter, 83, Holland Park Avenue, W.; William Arthur Williams, 75, High Street, Wapping, E.

The following candidates are recommended by the Council, under Bye-law I. (3):—Charles Robert Carroll, Hyderabad, Deccan, India; William Lash Miller, B.A., Ph.D., the University of Toronto; Frederick Louis Wilder, Villa Nova de Lima, Minas Geraes, Brazil.

The following papers were read:—

133. "*Determination of the Constitution of Fatty Acids.*" Part I. By Arthur W. Crossley and Henry R. Le Sueur.

The paper gives a detailed account of experiments undertaken with the idea of devising a method for the determination of the constitution of fatty acids. An acid, $CH_2X{\cdot}CH_2{\cdot}CO_2H$, is first converted into the ethylic salt of the monobromo-derivative, $CH_2X{\cdot}CHBr{\cdot}CO_2Et$, which is then treated with quinoline or diethylaniline, whereby the elements of hydrogen bromide are removed, and the ethylic salt of an unsaturated acid of the acrylic series, $CHX{:}CH{\cdot}CO_2Et$, is produced. The acid obtained by hydrolysing this salt is oxidised with potassium permanganate, giving rise to the corresponding dihydroxyacid, $CHXOH{\cdot}CHOH{\cdot}CO_2H$, which is then oxidised with chromic acid, with the production of the acids $X{\cdot}CO_2H$ and $CO_2H{\cdot}CO_2H$. A fatty acid (or ketone) containing two carbon atoms less than the original acid has thus to be identified, and as the number of isomerides decreases greatly with loss of two carbon atoms, the possibility of identification is much enhanced.

The method has been carried out with valeric, isovaleric, and isobutylacetic acids with good results, the products identified being propionic acid, acetone, and isobutyric acid respectively.

The authors propose to continue the investigation with higher fatty acids, such as ethylisopropylacetic and stearic acids, and with a dibasic acid, such as pimelic (isopropylsuccinic) acid.

134. "*The Crystalline Form of Iodoform.*" By William Jackson Pope.

Considerable difficulty is experienced in obtaining iodoform in well developed crystals from solutions in the ordinary organic solvents, but it separates from acetone in magnificent six-sided tablets belonging to the hexagonal system. The crystals exhibit the forms $c\{111\}$, $r\{100,\ 22\bar{1}$, $p\{\bar{1}10\}$, and $m\{2\bar{1}\bar{1}\}$, and have the axial angle $\alpha = 93° 41'$; the double refraction is negative in sign and strong.

135. "*The Characterisation of Racemic Compounds.*" By Frederic Stanley Kipping and William Jackson Pope.

Having previously shown that crystallographic data afford a sure basis for the characterisation of racemic compounds, the authors now give the results of their examination of a method suggested and made use of by Ladenburg for this particular purpose.

Ladenburg stated (*Ber.*, 1894, 27, 3065) that if, on fractionally crystallising a mixture of an externally compensated substance with excess of one of the active constituents, the various fractions differ in specific rotation, the existence of a racemic compound is established; if, on the other hand, the various fractions have the same specific rotation, then the existence of a racemic compound is disproved.

The authors point out that the argument upon which Ladenburg's method is based is fallacious, and, further, on examining experimentally several cases of mixtures of an externally compensated substance with an excess of one of the optically active isomerides, they find that the method is valueless.

Mixtures of the non-racemic inactive sodium ammonium tartrate with the isomeric dextrotartrate, and of the racemic inactive sodium potassium tartrate with the corresponding dextrotartrate, were fractionally crystallised, and it was found that in each case the excess of dextrorotatory salt separated out first, most of the externally compensated substances remaining in the mother liquors.

136. "*The Occurrence of Orthohydroxyacetophenone in Chione Glabra.*" By Wyndham R. Dunstan and T. A. Henry.

The wood of *Chione glabra*, a large flowering tree indigenous to Grenada, has a strong aromatic, somewhat fœcal, odour. This is due to a volatile oil which the authors find is chiefly composed of *orthohydroxyacetophenone*, $C_6H_4Ac{\cdot}OH$. The oil also contains a minute amount of what appears to be the crystalline methyl ether of this substance, $C_6H_4Ac{\cdot}OMe$.

The properties of orthohydroxyacetophenone, prepared in the laboratory from orthonitrocinnamic acid as a starting point, agree precisely with those of the volatile oil of *Chione glabra*.

Discussion.

In reply to Dr. Harden, Professor Dunstan said that he thought the degradation of vegetable proteid a possible mode of origin of indole derivatives, though some botanists were of opinion that it was more probable that they resulted from simpler synthetic processes.

137. "*Preparation of Hyponitrite from Nitrite through Oxyamidosulphonate.*" By E. Divers and T. Haga.

The authors have already published, disconnectedly, the facts (1) that sodium nitrite can be very completely and easily changed into oximidosulphonate by dissolving it with the calculated quantity of sodium carbonate, and passing sulphur dioxide into the solution; (2) that sodium oximidosulphonate can be hydrolysed very exactly into oxyamidosulphonate; and (3) that sodium oxyamidosulphonate can be largely decomposed into hyponitrite and sulphite by dissolving much potassium hydroxide in its concentrated solution. Details are now given by which, taking advantage of these facts, sodium nitrite can be converted into 60 per cent of its equivalent of silver hyponitrite. The essential points are to keep the temperature at 0° during the sulphonation of the nitrite; to allow the oximidosulphonate to hydrolyse, in the absence of sulphite, at or near the common temperature, during about 24 hours, so as to produce only oxyamidosulphonate and acid sulphate; to neutralise the solution by alkali carbonate, then dissolve in it sufficient potassium hydroxide to make the solution one of about equal weights of the hydroxide and water (having taken care from the first to use as little water as possible), and allow the whole to stand during 30 hours; to fractionally precipitate the hyponitrite by silver sulphate (or nitrate) from the greatly diluted alkaline solution, leaving the sulphite and the alkali in solution; to separate the silver hyponitrite from the metallic silver, &c., which accompanies it, by dissolving it in very cold dilute sulphuric acid, then filtering, and finally neutralising the sulphuric acid by sodium carbonate with the greatest expedition. Some oxyamidosulphonate always escapes decomposition by the potassium hydroxide; of that decomposed about 80 per cent becomes hyponitrite, and the rest nitrous oxide and alkali, besides, of course, sodium sulphite in either case.

138. "*Absorption of Nitric Oxide in Gas Analysis.*" By E. Divers.

A concentrated alkaline solution of sodium or potassium sulphite absorbs nitric oxide completely and quickly, forming with it alkali (hypo)nitrososulphate, and can be used in gas analysis with satisfactory results.

139. "*Interaction of Nitric Oxide with Silver Nitrate.*" By E. Divers.

Silver nitrate decomposes freely in a current of nitric oxide at much lower temperatures than when heated in air or carbon dioxide. The products, apart from oxygen, are the same, namely, nitric peroxide, silver, and silver nitrite, except that the silver nitrite is, for a time, an abundant product in presence of nitric oxide, whereas in its absence, when the temperature of decomposition is much higher, only a little of the nitrite is ever found, because it passes probably into nitric peroxide and silver nearly as fast as it is produced.

Either nitric oxide acts directly upon the silver nitrate, or, what is more probable, the imperceptible decomposition of silver nitrate alone, at temperatures of 220—250°, into oxygen and nitrite becomes rapid and marked in presence of nitric oxide, in consequence of the latter taking up oxygen as fast as it is formed by the decomposing nitrate.

Nitric oxide has no effect on heated sodium, potassium, barium, and lead nitrates.

140. "*Preparation of Pure Alkali Nitrites.*" By E. Divers.

Alkali nitrites are easily obtained pure and in concentrated solution by passing nitrous gases containing slight excess of nitric oxide into concentrated solutions of pure potassium or sodium hydroxide or carbonate, out of contact with air. With ordinary care no nitrate is formed; it is a current mistake to suppose that it is.

Both nitrites are slightly yellow, and their concentrated solutions markedly yellow. The sodium salt melts at 213°; at 15°, six parts of water dissolve five parts of it. Its crystals are often very large, but very thin, flattened prisms, moderately deliquescent. Sodium nitrite can be readily purified by re-crystallisation; potassium nitrite cannot. Potassium nitrite occurs only in minute, short prisms, and is soluble in one-third of its weight of water. It is exceedingly deliquescent, but its crystals are actually anhydrous, although Lang and Hampe independently found them to contain $\frac{1}{2}H_2O$.

Discussion.

Mr. Groves remarked that sodium nitrite is manufactured on a large scale for use in the colour industry, and is sent into the market nearly pure, containing some 98 per cent of the salt, but as far as his experience went neither the salt nor the solution is yellow.

He had found that when arsenious anhydride is heated at 70° with nitric acid of sp. gr. 1·3, nearly pure nitrous anhydride, mixed only with a little nitric oxide, is evolved, and that a dilute solution of nitrous acid could readily be prepared by passing this vapour into water at 0° containing some crushed ice.

141. "*The Reduction of an Alkali Nitrite by an Alkali Metal.*" By E. Divers.

Nitrous oxide, nitrogen, hydroxylamine, ammonia, sodium hyponitrite, and sodium hydroxide are invariably products of the reduction of sodium nitrite by sodium amalgam, but the process can be modified so that each of them in turn shall be formed in any desired quantity between a very small amount and a certain maximum. The principal points needing attention are the degree of concentration of the solution and the temperature at which the reduction takes place.

The quantity of hyponitrite will be equivalent to more than one-sixth of the nitrite when the solution is concentrated and is not allowed to grow too hot; by large dilution, alone or aided by heat, it can be made indefinitely small. That of hydroxylamine may be made to be anything between one-eleventh and one three-hundredth of the equivalent of the nitrite, sufficient dilution and cooling being the conditions for a high yield of hydroxylamine. Ammonia being merely reduced hydroxylamine, its yield depends on that of hydroxylamine and reduction of this by the further action of the amalgam. The temperature at which the reduction is allowed to proceed determines how much of the gaseous products shall be nitrous oxide and how much nitrogen, high temperature causing the production of nitrogen. The two gases together are always nearly equivalent to a little more than four-fifths of the nitrite.

Sodium amalgam is entirely without action upon sodium hyponitrite. It has always very little action, if any, upon nitrous oxide at the common temperature. Sodium hyponitrite in concentrated sodium hydroxide solution is very stable and may be heated at 100° without effervescing. During the reduction of the nitrite, the gases produced may be seen to come exclusively from the surface of the solution touching the amalgam. As already indicated, the production of nitrous oxide and of nitrogen is at the expense one of the other, not at that of the hyponitrite or hydroxylamine. Similarly, the hyponitrite and hydroxylamine increase each at the expense of the other. Yet it does not seem that the nitrogen is produced by reduction of the nitrous oxide, and certainly the hydroxylamine is not a reduction product of the hyponitrite. It also does not seem that the nitrous oxide comes from the decomposition of the sodium hyponitrite to any important extent.

Sodium nitrite, reduced by sodium amalgam, passes, it would seem, first into the unknown transition products, NaNO and NaON, to the extent of four-fifths into the former and one-fifth into the latter. From the latter, or sodioximide radicle, the hyponitrite will be formed by condensation when the alkali solution is concentrated, and the hydroxylamine by reduction when the alkaline solution is dilute. From the former, or sodium nitroside radicle, the nitrous oxide will be produced by condensation and hydrolysis at low temperatures, or the nitrogen by reduction, condensation, and hydrolysis, at high temperatures.

The reduction of potassium nitrite by potassium amalgam proceeds closely on the same lines as that of sodium nitrite by sodium amalgam.

142. "*Hyponitrites; their Preparation by Sodium or Potassium and Properties.*" By E. Divers.

Sodium nitrite reduced in concentrated solution by sodium amalgam, yields a third of its weight of silver hyponitrite, and nearly the equivalent amount of several other hyponitrites, without the need of this salt as an intermediary. In this respect, the process has an advantage over the oxyamidosulphonate method. The hydroxylamine, which always accompanies the sodium hyponitrite, is easily got rid of by the continued action of the sodium amalgam, which is without action on the hyponitrite itself. The resulting ammonia is removed by exposure of the solution over sulphuric acid for a night under reduced pressure. Mercuric oxide, employed by all other chemists to remove hydroxylamine, has the fault of regenerating nitrite. The concentrated solution of sodium hyponitrite and hydroxide, thus obtained, is remarkably stable. In the preparation from it of other salts than the sodium salt itself and the silver salt, the sodium hydroxide has first to be neutralised, after diluting the solution with ice and water, mercurous nitrate being employed as an indicator with portions of the solution.

Sodium hyponitrite is prepared from the most concentrated alkaline solution, obtained as above, by precipitation with absolute alcohol, or (Jackson) by evaporation in a vacuum and washing the salt with alcohol. It forms minute, crystalline granules, $(NaON)_2+5H_2O$, which effloresce and evolve nitrous oxide in the air, but in a vacuum desiccator are converted into an anhydrous non-coherent powder, stable in dry air. The anhydrous salt bears a somewhat high temperature in dry air without decomposition, then fuses and effervesces, forming sodium oxide, sodium nitrite, and nitrogen. According to Prof. Ikeda, sodium hyponitrite gives numbers for its molecular magnitude approximating to those required for $(NaON)_2$ by Lowenherz's cryoscopic method.

Silver hyponitrite is prepared by adding a highly dilute solution of silver sulphate or nitrate to the alkaline solution already described. It decomposes exceedingly slowly in the moist state, forming products similar to those obtained on heating. It is also decomposed by bright light, becoming brown, but is not blackened, by the light alone. When heated, it is decomposed without explosion, its yellow colour changing directly to that of metallic silver, without intermediate darkening; the products are silver, silver nitrate, nitrogen, nitric oxide, and nitric peroxide. A study of the change renders it most probable that the nitric oxide and silver nitrate are not primary products, but arise from interaction between the nitric peroxide and undecomposed hyponitrite. Sodium chloride solution digested with excess of silver hyponitrite has only 25/43 of its chlorine displaced by the hyponitrite ion. Paal's supposed silver nitrito-hyponitrite, $Ag_2N_2O_3$, appears not to exist.

The preparation and properties of mercuric, mercurous, cupric, lead, barium, strontium, calcium, and potassium hyponitrites are described. Cuprous hyponitrite could not be obtained, nor were Rây's basic mercuric compounds met with. Maquenne's hypo-isonitroso-acetates were examined, and the formula—

$$OAc \cdot Ca \cdot O \cdot N_2 \cdot OAc, Ca(OAc)_2, 5H_2O$$

is suggested for the calcium salt.

Hyponitrous acid, in solution, is more acid to litmus paper than carbonic acid, but its effect disappears as the paper dries. It decomposes slowly into nitrous oxide and water (and nothing else except a trace of nitrous acid having another origin). When pure, it has no action on iodine-water or with the starch-iodide test. It decomposes silver carbonate, sulphate, nitrate, and chloride, when present in excess, but not the iodide. It is easily oxidised, but is unaffected by reducing agents. Apparently it has not yet been obtained free from every trace of nitrous acid; when carefully prepared, it will remain, however, for more than an hour without producing a blue colour with the starch-iodide test. Hyponitrous acid can be estimated gravimetrically as the silver salt, and volumetrically by potassium permanganate. Thum's permanganate process, in which the hyponitrous acid becomes ultimately nitric acid, is an excellent one; the failure of Hantzsch and Sauer and of Kirschner in its use is due to the modifications they made in it.

Discussion.

Professor **Dunstan** remarked that Dr. Divers in the present series of papers had cleared up a number of doubtful points. In connection with the formation of hyponitrite by the reduction of nitrite in aqueous solution, Dr. Divers had confirmed the observations made in 1887 by Mr. Dymond and himself, as to the simultaneous production of hydroxylamine and its non-formation by the further reduction of hyponitrite. He still adhered to the view that they put forward that these results were best explained by the assumption that the nitrite was first hydrogenated, forming a compound of the formula $NaN(OH)_2$, which on the one hand loses water, forming hyponitrite, and on the other is hydrolysed, forming sodium hydroxide and dihydroxylamine, $NH(OH)_2$, which by further reduction furnishes hydroxylamine.

Mr. G. N. **Huntly** pointed out that the hypothesis of the formation of dihydroxylamine, as a first reduction product, suggested by Professor Dunstan, had the advantage of being equally applicable to the two other methods of preparing hyponitrites, viz., from sodium hydroxylaminesulphonate (Divers) and benzenesulphohydroxamic acid (Piloty), by the action of concentrated potash. The three reactions on this hypothesis would be represented as follows:—

1. $NH(OH)(SO_3Na)+KOH=KNaSO_3+NH(OH)_2$;
2. $NH(OH)(SO_2 \cdot C_6H_5)+KOH=C_6H_5 \cdot SO_2K+NH(OH)_2$;
3. $HO \cdot NO+2H=NH(OH)_2$.

In alkaline solution, the dihydroxylamine would condense thus—

$$OH \cdot NH \cdot OH+H(OH)N \cdot OH=OH \cdot N{:}N \cdot OH+H_2O,$$

and there being no tendency to condensation in acid solution, further reduction should give hydroxylamine, a conclusion in accordance with the facts observed by Professor Divers.

143. "*Paranitro-orthanisidine.*" By Raphael Meldola, F.R.S.

As paranitro-orthanisidine (m. p. 139—140°), which was described in a paper published in conjunction with Messrs. Woolcott and Wray (*Trans*, 1896, vol. lxix., 1330), has recently been made the subject of a patent by the Fabriques de Produits Chimiques de Thann et de Mulhouse (Germ. Pat., 98637 of 1897), the author records some further observations which have been made with the substance, as it is proposed to continue its investigation.

The acetyl derivative, purified by repeated crystallisation from water so as to get rid of the isomeric metanitro-derivative simultaneously formed, melts at 153—154°, the melting point 143—146° given in the former paper being that of the mixed isomerides. The acetyl-derivative of *p*-nitro-*o*-anisidine can be reduced by dissolving in hot water and agitating with iron dust and a little acetic acid. The *p*-amido-*o* acetanisidide thus formed is somewhat unstable, and has not yet been isolated. It is readily diazotisable, and the NH_2-group has by this means been replaced by iodine with the formation of p *iodo o-acetanisidide*, [NHAc : OMe : I = 1 : 2 : 4]. This compound crystallises in beautiful silvery scales melting at 175—176°.

0·1778 gave 74 c.c. moist nitrogen at 19° and 764 mm. N = 4·80.

0·202 gave 0·1618 AgI. I = 43·28.

The formula requires N = 4·81 per cent; I = 43·64 per cent.

Mr. Frederick Henry Streatfeild was assisting in this investigation, but having left to accept an appointment elsewhere, the work was temporarily interrupted.

NOTICES OF BOOKS.

Government Agricultural Experimental Station for North Dakota. — Bulletin No. 32. Fargo, North Dakota. 1898.

This Bulletin deals with five subjects, viz., drinking water, wool scouring, soil humus, analysis of foods, and vinegar. With regard to the water question, the permissible amount of total solids is here discussed; a considerable difference of opinion is shown by different authorities,—one puts the amount permissible at 57·5 parts per 100,000, another says the safe limit is only 30 parts, but that 100 parts should condemn the water.

A number of supplies to large cities in the United States show a variation between 4·7 and 34 parts per 100,000, but too much weight should not be given to such figures, as the composition of the dissolved matter must most materially influence its power for good or evil, this again depending to some extent on the constitution of the individual. A further list of twenty water supplies is also given, all of which contain considerable amounts of sulphate of sodium (Glauber's salts); the continued use of such waters cannot but be considered as harmful.

The subject of humus in soils is also carefully considered, and some very interesting data are given, the summary of results showing that continuous wheat growing seriously impoverishes the soil; as much as five pounds of organic matter is lost for every pound which goes to furnish nitrogen for the wheat. By the loss of humus the soil becomes less retentive of moisture, and gives it up much more readily by evaporation; burning the stubble again destroys much organic matter and humates. The best way to keep up the supply of humus in the soil is to imitate Nature, and, for the present, grow at least one crop in five of grass; clover would be an ideal crop to maintain the supply of humus, and also to aid in collecting nitrogen from the air, but any grass will serve to supply humus.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvii., No. 13, September 26, 1898.

Action of Lime and Calcium Carbonate on certain Natural Earthy Substances.—G. André.—The author has already indicated the possibility of determining the constitution of natural humic substances by examination of the nitrogenous products generated on treatment with potash and hydrochloric acid respectively. In the present paper a description is given of the treatment of similar specimens of earths with lime, with chalk, and with water. The results of estimation of the nitrogen in the products obtained are tabulated. It is observable that, in the case of each specimen, less nitrogen was evolved as ammonia under the influence of lime than was previously evolved under the influence of potash. The same remark applies to the amount of nitrogen found in soluble form in the lime liquor after filtration. The actions of chalk and of water give less significant results. In the case of exclusively acid soils (turf, heather-mould) it would be necessary to find another agency by which the amides of the soil may be brought into soluble form, in order to explain how this organic nitrogen changes to the ammonia which is necessary to the plants. Apparently the action of microbes alone is at work, since the presence of mineral bases cannot be taken into consideration; or the plants growing in acid soils may be capable of absorbing certain oxides directly, without transformation of the latter into ammoniacal salts.

No. 14, October 3, 1898.

Analysis of some Samples of Commercial Calcium Carbide.—Henri Moissan.—Usually calcium carbide is prepared commercially from coke, which contains large quantities of mineral matter. The chalk also which is used in its manufacture often contains silicates of aluminium, and various phosphates and sulphates. The carbide, therefore, has for impurities phosphide of calcium, sulphide of aluminium, besides various silicides,—consequently the addition of water produces, besides acetylene gas, both phosphoretted and sulphuretted hydrogen. These impurities are one of the greatest difficulties when acetylene is used for lighting purposes. Commercial carbide, of which 1 kilo. should give 349 litres of acetylene theoretically, gave, in the seven samples examined, from 292·8 to 318·7 litres. These numbers are lower still if the carbide is not crystalline, but porous and of a greyish colour. Ammonia and nitrogen were also found in the gas. In order to study the insoluble residue from the carbide, the latter was decomposed by sugar solution, so that the chalk remained in solution, and the residue could be collected. This was found to consist of carbon, calcium and iron silicides.

Preparation and Properties of Double Carbides of Iron and Chromium, and of Iron and Molybdenum.—P. Williams.—The author has prepared the two new double carbides, $3Fe_3C.2Cr_3C_2$ and $Fe_3C.Mo_2C$. These carbides, as in the case of the previously described double carbide of iron and tungsten, can be considered as compounds of carbide of iron, Fe_3C, and the metallic carbides prepared by M. Moissan in the electric furnace. It is remarkable that this double carbide of iron and chromium, $3Fe_3C.2Cr_3C_2$, enters into the same series as those compounds $3Fe_3C.Cr_3C_2$ and $Fe_3C.3Cr_3C_2$, isolated by A. Carnot and Goutal. There is always a certain relation between the carbide produced and the quantity of free graphite present. The quantity of carbide is, in some measure, inversely proportional to the quantity of free graphite. The method of cooling the crucible also influences the proportions, as has already been shown by Moissan in the production of carbide of iron in the electric furnace.

New Combinations of Phenylhydrazine with certain Metallic Salts.—M. Pastureau.—M. Schyerring, in 1893, discussed the combinations of phenylhydrazine with the sulphates of the metals of the magnesium series, and in 1897 M. Moitessier extended this study to the principal salts of this series—chlorides, bromides, iodides, acetates. The present paper describes the preparation and properties of compounds of phenylhydydrazine with bismuth chloride ($BiCl_3.6[N_2H_3C_6H_5]$), with bismuth nitrate ($Bi(NO_3)_36[N_2H_3C_6H_5]$), with zinc sulphite—

$$(ZnSO_3.2[N_2H_3C_6H_5]),$$

and with manganese sulphite ($MnSO_3.2[N_2H_3C_6H_5]$).

MEETINGS FOR THE WEEK.

Tueeday, 27th, Thursday, 29th, Saturday, 31st.—Royal Institution, 3. (Christmas Lectures). "On Astronomy," by Sir Robert Stawell Ball, F.R.S., &c.

THE CHEMICAL NEWS.

Vol. LXXVIII., No. 2040.

THE ORIGIN OF THE GASES EVOLVED ON HEATING MINERAL SUBSTANCES, METEORITES, &c.*

By MORRIS W. TRAVERS, D.Sc.

(Concluded from p. 307).

Meteorites.

It has long been known that considerable quantities of gas are evolved when meteorites are heated *in vacuo*. The gas usually consists of hydrogen, carbone monoxide, carbon dioxide, and hydrocarbons, in varying proportions, and attempts have been made to draw conclusion as to the origin of different meteorites from the results of analysis of the gases obtained by heating them. These speculations are based upon the supposition that the gases evolved on heating are present as such in the meteorite, occluded from the atmosphere in which it previously existed.

Beyond the gases already mentioned, the results of many observers appear to show that nitrogen is also invariably present. Among those that I have examined the gas evolved on heating contained, in no single instance, a trace of nitrogen (*Roy. Soc. Proc.*, 1897, vol. lx., p. 442). Graham (*Roy. Soc. Proc.*, 1867, vol. xv., p. 502) found as much as 10 per cent of nitrogen in the gas from the Lenarto meteorite, and Mallet (*Roy. Soc. Proc.*, 1872, vol. xx., p. 365) found 10 per cent of nitrogen in the gas from a meteorite from Augusta Co., Virginia. Wright (*Amer. Journ. Sci.*, [3], vol. ix., pp. 294 and 459; vol. x., p. 44; vol. xi., p. 254) examined a large number of meteorites, and found that in almost every case the gas contained nitrogen. In this case, however, the presence of nitrogen can easily be accounted for, as no particular precautions were taken with regard to the thorough exhaustion of the apparatus employed. A Sprengel pump was used, "which was kept running till the air was thoroughly removed, *as could be seen by the gauge.*" Dewar (*Roy. Inst. Proc.*, 1886, p. 545) found nitrogen, in quantities not exceeding 4 per cent of the total gas, in the gases from samples of meteorites and graphite.

In one single case a meteorite has been found to yield a trace of helium on heating (*Nature*, 1896).

With regard to the carbon dioxide and combustible gases, it is difficult to obtain direct evidence as to their origin. In the case of meteorites containing bituminous matter and carbonaceous nodules, the evolution of these gases may be attributed to the destructive distillation of their constituents. Meteorites of the stony variety appear to evolve more carbon dioxide and hydrocarbons, and less hydrogen and carbon monoxide, than those which are of a metallic nature. Several specimens of stony meteorites have been carefully examined by Wright and Dewar with the following results:—

Wright (*loc. cit.*) found that in the case of a stony meteorite from Iowa Co., Iowa, the carbon dioxide was given off at a very low temperature. The following table shows the composition of the gas given off at different temperatures:—

	At 100°.	At 250°.	Below red heat.	Dull red heat.	Full red heat.
CO_2	95·46	92·32	42·27	35·82	5·56
CO	0·00	1·82	5·11	0·49	0·00
H_2	4·54	5·86	48·06	58·51	87·53
N_2	0·00	0·00	4·56	5·18	6·91

The meteorite lost about 10 per cent of its weight of water on heating. The water was allowed to collect in the apparatus, and as no drying reagent was used, it is easy to account for the presence of hydrogen in the gas. The carbon dioxide may have been present as an unstable hydrated carbonate, or in the state of occlusion in the pores of the substance.

Dewar (*loc. cit.*) showed that a meteorite of a similar nature was capable of re-absorbing water and carbon dioxide after the gases had been removed by heating *in vacuo*. The following results were obtained:—

	Gas in volumes of meteorite.	CO_2.	CO.	H_2.	N_2.
After 24 hours ..	0·61	54·0	—	42·4	3·6
After 6 days more..	2·47	47·0	5·0	47·0	1·0
After 8 days more..	0·63	96·1	2·0	1·5	—

The quantity of water re-absorbed after the second heating was very small, and it is interesting to note that the quantity of hydrogen evolved during the subsequent heating was also very small. From this it would appear that the hydrogen was produced directly from the water. There is no evidence to show whether the carbon dioxide entered into combination with some constituent of the meteorite or not.

Meteorites of the second class usually consist chiefly of metallic iron, nickel, &c., with small quantities of crystalline minerals, such as olivine. The presence of these minerals, which are usually hydrated silicates containing ferrous oxide, might in themselves account for the formation of hydrogen. The carbon monoxide might be produced by the interaction of carbon dioxide, the product of decomposition of a carbonate, with the metallic iron. The small quantities of hydrocarbon, which are also present in the gas, and which appear to belong to the saturated series, might be produced by the action of water, which is invariably present, upon metallic carbides. The changes which take place are probably of a complicated nature.

In order to ascertain whether a sample of meteoric iron actually contained occluded or enclosed gases, the following experiment was performed. A piece of meteoric iron was cut into fine shavings, which were carefully cleaned. The metal was divided into two portions; one part was heated in a sealed tube with copper sulphate and water, in the manner already described, the other was heated *in vacuo*. The gases evolved were in each case collected and analysed.

	By action of heat.	Copper sulphate experiment.
Hydrogen	0·322 c.c. per grm.	0·014
Carbon monoxide and hydrocarbons ..	0·164 ,, ,,	
Carbon dioxide	2·222	0·739

The trace of hydrogen which was produced during the copper sulphate experiment may well be attributed to secondary relations between the metal and the salts in solution.

It would appear then that the gases produced by the action of heat upon meteorites are not present as such, but are the products of decomposition of their non-gaseous constituents. It is therefore impossible to draw conclusions as to the former history of a meteorite from the nature of the gases which it gives on heating.

Helium and Argon.

With regard to the state in which helium is present in the minerals from which it is obtained by the action of heat, there is at present no conclusive evidence. It must be present under one of three conditions:—

I. In combination with some constituent of the mineral.
II. Occluded; or in solution in the mineral.
III. Enclosed in cavities under pressure.

Microscopic examination of the minerals, from which

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* A Paper read before the Royal Society, November 24, 1898.

helium has been derived, has failed to reveal the presence of cavities, and, indeed, if we assume that cavities exist, and that they contain all the helium present in the mineral, we have to make further assumptions to explain why the helium escapes when the mineral is heated, although in most cases no disintegration takes place. It seems improbable that the helium is present in the state of solid solution or occlusion, a condition of which we yet know little, for unless we assume that the rate of diffusion of the helium through the mineral in which it is dissolved is infinitely small, the gas should long have escaped into the atmosphere. Further, it is probable that the supposed cases of solution of gases, like hydrogen, in solids such as platinum, palladium, &c., are really cases of chemical combination, as has recently been proved by the researches of Ramsay, Mond, and Shields, and even in meteoric iron it is improbable that the hydrogen is not present as such, but is the product of secondary reactions. Indeed, in the state of our knowledge at present it is impossible to draw a distinction between occlusion and chemical combination.

We are, therefore, forced to the conclusion that helium is present in the minerals in the state of combination with one of its constituents. It may be well to review such positive evidence as exists in favour of such a supposition.

In the first place the gas is not found generally dispersed among crystalline mineral substances, but seems only associated with certain elements, uranium, yttrium, &c., in minerals which are invariably vein products.

It has been pointed out by Professor Ramsay and the author (*Roy. Soc. Proc.*, vol. lxii., p. 325), that in certain cases the evolution of helium from the mineral is accompanied by a considerable evolution of heat, and in one case by a considerable decrease in density. This matter has been dealt with fully in the paper (*loc. cit.*), and is considered as evidence in favour of chemical combination. Julius Thomson (*Zeit. Phys. Chem.*, vol. xxv., p. 112), has confirmed this observation.

A series of experiments were undertaken to determine the conditions under which the minerals gave off helium. It was found that from cleveite helium was evolved, but very slowly, at the temperature of boiling quinoline, and somewhat faster at the temperature of boiling sulphur. At a bright red heat a considerable quantity of helium was obtained, but in no case did the mineral lose the whole of its helium under the influence of heat alone.

By heating cleveite to redness for some hours a mixture of helium, hydrogen, carbon dioxide, and carbon monoxide was obtained; the gas came off readily at first, and appeared finally to cease altogether.

A quantity of the same sample was completely decomposed by means of sulphuric acid (30 per cent) in an exhausted sealed tube. The results are given below:—

	By heating the mineral.	By action of sulphuric acid.
He ..	1·487 c.c. per grm.	3·201 per cent per grm.
H_2 ..	0·367 "	0·333 "
CO_2 ..	2·298 "	

It will be noticed that only half the helium is given off on heating the mineral; this makes it appear probable that if the helium is present in the mineral originally in a state of binary combination the decomposition takes place according to the equation:—

$$XHe_2 = XHe + He.$$

A specimen of fergusonite was also examined, but the results were not altogether satisfactory, as it was found to be practically impossible to completely decompose the mineral by the action of 30 per cent sulphuric acid; strong sulphuric acid appeared to be still more inactive. When fused with acid potassium sulphate a larger yield of helium was obtained, but the mineral was not completely decomposed. The following figures indicate that about half the helium contained in the mineral is liberated under the influence of heat:—

	By action of heat on mineral. C.c. per grm.	By 30 per cent sulphuric acid. C.c. per grm.	Fusion with acid sulphate. C.c. per grm.
He	1·041	1·434	1·813
H_2	0·231	0·163	
CO, &c. ..	0·326		

It is somewhat significant that both cleveite and fergusonite yield hydrogen when decomposed by sulphuric acid. If the helium were present in combination with a metal it would eventually be liberated as a hydride. It is probable that the hydride would be a very unstable compound and would decompose at the moment of formation.

Part of the hydrogen would probably be taken up by the ferric and uranic compounds, and part would escape in the gaseous state. A similar reaction would take place between sulphuric acid, and an iodide, in the presence of a reducible substance, at a higher temperature.

Conclusions.

It would appear that the only evidence on which the assumption that gases of a permanent character, such as hydrogen, carbon monoxide, nitrogen, helium, and argon, exist in the free state in the mineral substances from which they are evolved on heating, rests on certain observations with regard to the cavities which can sometimes be detected by microscopic examination.

The cavities may be either apparently empty or they may contain liquid, and when the mineral is warmed the liquid disappears at a temperature which is a few degrees below the critical point of carbon dioxide or of some hydrocarbon. The fact that the critical temperature of the liquid is a little below the point corresponding to carbon dioxide, in the case of a mineral containing that substance is not, however, of very great significance as pointing to the presence of a permanent gas. A small quantity of methane would produce the same result (Kuenen, *Phil. Mag.*, 1897).

Further, although it can be shown that *compact* minerals do enclose carbon dioxide and hydrocarbons, gases which can easily be liquefied, the analogy cannot be extended to gases such as hydrogen and helium in connection with minerals like chlorite, mica, and cleveite, which exhibit many cleavages.

On the other hand, there is, as I have endeavoured to show, a considerable amount of evidence in favour of the theory which I have put forward:—That in the *majority of cases* where a mineral substance evolves gas under the influence of heat, the gas is the product of the decomposition or interaction of its *non-gaseous* constituents at the moment of the experiment. The results of such experiments cannot, therefore, serve as basis for speculation as the origin and history of the substances in question.

ON THE
PREPARATION OF THE SILICIDES OF TUNGSTEN, MOLYBDENUM, CHROMIUM, AND MANGANESE.

By **H. N. WARREN**, Principal, Liverpool Research Laboratory.

In order to prepare the above-named compounds a quantity of graphitoidal silicon was obtained by fusing together, at a white heat, a mixture consisting of two parts of mineral cryolite and one of sodium silicate; when perfectly liquid, an ingot of aluminium 2 lbs. in weight was introduced into the mass, in order to set free the silicon. Reduction by this means always proceeds tranquilly, although attended with considerable rise in temperature, and in this respect differs greatly to when potassium silicofluoride is employed, the reaction in the latter instance often amounting to explosive violence, and resulting in a serious accident some four years previous, when operating upon a cwt. of melted silicofluoride at the Research Laboratory.

After fusion the silicon, if properly reduced, is found in the form of a perfectly spherical ingot, containing about 10 per cent free aluminium; this is separated by digestion in hot HCl, pure graphitoidal silicon remaining, which after drying should be finely pulverised. Manganese silicide is readily produced by reducing any of the oxides of manganese, in contact with an excess of silicon at a full white heat, the regulus thus procured presenting itself in the form of a well-melted ingot, and possessing a full white metallic lustre. It is very brittle, and readily scratches glass, being soluble with difficulty in ordinary acids, but readily attacked by means of hydrofluoric; it contains on an average from 30 to 40 per cent of silicon.

The chromium compound much resembles the manganese product, but is less readily attacked by reagents and somewhat less fusible, but at the same time possessing greater hardness.

For the preparation of the tungsten and molybdenum silicides a somewhat higher temperature is required, and the author recommends with confidence, in order to carry out the smelting operation, a small oxyhydrogen blast-furnace. An intimate mixture with either oxide of tungsten or molybdenum is next procured, and the furnace urged to its maximum heat, for about twenty minutes, the mixture being lodged in a specially prepared crucible. If the operation has been satisfactorily conducted a well-melted ingot is obtained, containing upwards of 20 per cent silicon, while in other cases, if the heat has been deficient, a metallic half-fused mass, containing various percentages of silicon, is the result. As regards their physical properties, the silicides of either tungsten or molybdenum appear to be highly crystalline and possessed of extreme hardness, some specimens even scratching rock crystals,—comparatively speaking, the tungsten compound ranking as the hardest.

All are with difficulty acted upon by acids, except hydrofluoric acid, whilst at a red heat chlorine attacks all of them readily. No electrical furnaces are required.

Liverpool Research Laboratory,
18, Albion Street, Everton, Liverpool.

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending November 30th, 1898.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To Major-General A. De Courcy Scott, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, December 10th, 1898.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Nov. 1st to Nov. 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined by us during the month, one was found to be "slightly turbid"; the remainder were all clear, bright, and well filtered.

The rainfall at Oxford during November has again shown a deficiency; the actual fall was 1·86 inches. The average fall for the past thirty years is 2·42 inches; this leaves a deficiency of 0·56 inch, and makes the total deficiency for the year 6·67 inches, or 28·2 per cent.

Our bacteriological examinations of 256 samples have given the results recorded in the following table; we have also examined 44 other samples, from special wells, standpipes, &c., making a total of 300 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	862
New River, filtered (mean of 26 samples) ..	80
Thames, unfiltered (mean of 26 samples) ..	7425
Thames water, from the clear water wells of five Thames-derived supplies (mean of 126 samples)	49
Ditto ditto .. .. highest	435
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 26 samples) ..	944
River Lea, from the East London Company's clear water well (mean of 26 samples) . ..	11

The bacteriological results for the month have been satisfactory. The East London water supply has been exceptionally good, the average of 26 samples being only 11 microbes per c.c., whereas the mean of 126 samples from the Thames-supplied Companies is 49 per c.c. Both these results prove highly efficient filtration; but it must be confessed that a reduction of the number of microbes to anything as low as 10 or 11 is highly exceptional, and more than could have been expected a few years ago, when between 100 and 200 microbes per c.c. were considered allowable in a potable water.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

A SCHEME FOR THE RAPID ANALYSIS OF BOILER WATERS FOR SCALE-FORMING INGREDIENTS.

By THOS. B. STILLMAN, M.Sc., Ph.D.

The complete analysis of a boiler water presents no difficulties to the analytical chemist, but the time required for the various separations and determinations of the constituents therein often precludes many examinations. Where the chemical analysis is desired for the amounts of the scale-forming ingredients only, a method should be used that is relatively rapid and approximately correct. A scheme embodying such a method whereby the amounts of calcium carbonate, calcium sulphate, magnesium carbonate, and iron oxide could be rapidly determined would be of great service in technical laboratories. In many railroad laboratories the following process is used to determine *total* scale-forming ingredients.

One-half litre of the boiler water is evaporated to dryness in a weighed platinum dish, and the amount of residue determined.

This residue is treated with a solution of alcohol 50 parts, and water 50 parts, and then filtered.

The undissolved matter is designated a scale-forming material.

This method gives, of course, the *total* matter that is scale-forming, but does not indicate the proportions of each constituent.

It is essential to know, in many cases, whether the scale will be calcium sulphate or calcium carbonate or magnesium carbonate.

Scheme for Rapid Analysis of Boiler Waters.

(Communicated to the writer by Prof. Wm. Main, Chemical Expert to New York Filter Co.).

Total solids. Mineral matter. Organic matter.	The desired amount of water is evaporated to dryness in a platinum dish and weighed; this residue (1) represents total solids. Ignite, then moisten slightly with distilled water, place in an atmosphere of carbonic acid for half an hour, dry and weigh; this residue (2) is the total mineral matter combined with carbonic acid, as it previously existed, before ignition. The difference in weight between Residue 1 and Residue 2 is the organic matter.
Scale-forming ingredients.	Extract soluble matter from Residue 2 with successive small portions of distilled water, in all 50 c.c. or less. Filter through ashless filter; dry the residue adhering to platinum dish. Dry and ignite filter and return the matter it may have retained to the platinum dish, and weigh. The weight of this residue (3) represents the total scale-forming ingredients of the water.
Non-scale-forming ingredients.	The filtrate contains the alkalis and magnesia combined with sulphuric acid and chlorine. These may be determined if desired, but are not necessary in this operation. Their aggregate weight may be determined by subtracting Residue 3 from Residue 2.

<table>
<tr><td colspan="5">Treat Residue 3 with hot HCl and filter. Wash well.</td></tr>
<tr><td rowspan="5"><i>Residue.</i> Insoluble mineral matter. Dry, ignite, and weigh as such. SiO_2, &c.</td><td colspan="4"><i>Filtrate.</i>—Add ammonic hydrate in slight excess, boil, and filter.</td></tr>
<tr><td rowspan="4"><i>Residue.</i> $Al_2O_3.Fe_2O_3$. Dry, ignite, and weigh as such.</td><td colspan="3"><i>Filtrate.</i>—Add solution of ammonic oxalate in slight excess, set aside ½ hour. Wash with water containing ⅛ its volume of ammonic hydrate.</td></tr>
<tr><td rowspan="3"><i>Residue.</i> Dry, ignite, and weigh as CaO.</td><td colspan="2"><i>Filtrate.</i>—Add solution of sodic phosphate with constant stirring. Set aside ½ hour; filter, wash with water containing ⅛ its volume of ammonic hydrate.</td></tr>
<tr><td rowspan="2"><i>Residue.</i> Dry, ignite, and weigh as $Mg_2P_2O_7$ and calculate to MgO.</td><td><i>Filtrate.</i>—Acidify with HCl, add solution of $BaCl_2$ in slight excess, boil, set aside ½ hour, filter, wash well with hot water.</td></tr>
<tr><td><i>Residue.</i>—$BaSO_4$. Dry, ignite, and weigh as $BaSO_4$, and calculate to SO_3. This amount of SO_3 is combined with CaO to form $CaSO_4$ that exists in Residue 3.</td></tr>
<tr><td>SiO_2, &c.</td><td>$Al_2O_3.Fe_2O_3$.</td><td>CaO.</td><td>MgO.</td><td>SO_3.</td></tr>
</table>

The scale formed by calcium sulphate is hard, compact, and exceedingly difficult of removal, whereas the scale formed by calcium and magnesium carbonates is more or less porous and not difficult of removal.

A scheme of analysis, that has been used by the author, and showing many advantages for correct determinations with rapidity, is appended.

The remaining CaO, as well as the MgO, are calculated to carbonates and the amounts of $CaSO_4$, $CaCO_3$, $MgCO_3.SiO_2$, &c., and $Al_2O_3.Fe_2O_3$ should equal the weight of Residue 3. Professor Main states regarding the above scheme as follows:—

"Careful tests made with artificial mixtures of sulphate of lime and carbonate of lime show that the error due to solubility of calcium sulphate in water is hardly weighable, especially after it is converted into anhydrous sulphate by heat.

"The amount of sulphate of lime which will fail to precipitate from solution, and that which can be dissolved (in any reasonable time) from the solid state with pure water alone, are very different things. This supposed solubility has previously prevented chemists from using methods similar to the above scheme for a rapid method of boiler water analysis."—*The Stevens Indicator*, October, 1898.

Science Gossip.—After a successful career of over thirty years, *Science Gossip*, the favourite journal for amateurs devoted to natural, physical, and applied science, has just entered upon independent offices, at 110, Strand. This magazine has latterly been greatly improved, and the articles deal with subjects of most recent discovery or theory. The editorial management is still under the control of Mr. John T. Carrington, assisted by Miss F. Winstone. There are also several specialists as departmental editors for such sections as physics, microscopy, astronomy, botany, geology, zoology, meteorology, &c.

THE ACTION OF NITRIC ACID ON TIN IN THE PRESENCE OF THE METALS OF THE IRON GROUP.

By F. H. VAN LEENT.

While testing for lead in tin plate I had occasion to observe the reaction mentioned by Rose on the subject of the separation of tin from other metals by means of nitric acid. The tin coating of the sheet iron was scraped off with a hard steel knife, in such a manner that, besides the metal to be analysed, a relatively large proportion of iron was also detached. This mixture was treated with nitric acid of specific gravity 1·2, and at the end of the reaction the liquid was evaporated to dryness on the water bath. The residue moistened with water was completely dissolved. Rose points this out as a very interesting circumstance ("Analytische Chemie," ii., 284). It is, in fact, an exception to the rule, according to which we should expect to obtain the tin in the state of oxide and retain the iron in solution. To avoid this inconvenience in an analysis of bronzes containing iron and tin, Fresenius advises precipitating the tin with sulphuric acid or nitrate of ammonium in the solution of metallic chlorides obtained by successive treatments with nitric and hydrochloric acids ("Quantitative Analysis," i., 264, 265). With the object of discovering what compound of tin could have been formed, I treated mixtures of powdered iron and tin, either finely granulated or in small clippings, with nitric acid. I then evaporated to dryness and took up the residue with water. The formation of a nitrate of tin was hardly probable in view of the great instability of this compound, which is easily decomposed by heating. To obtain great solubility it is necessary, during the evaporation, to take care to mix the ferric nitrate, which adheres to the sides of the porcelain dish, with the stannic oxide which is found at the bottom.

In these experiments I have found that the minimum quantity of iron which will hold a convenient quantity of tin in solution is about one-fifth or one-sixth of the latter. Small quantities of iron, 0·03 grm. to 1 grm. of tin for example, dissolves only a small quantity of the other metal. With 0·05 grm. of iron a part of the stannic oxide is rendered soluble, and the viscous residue is very difficult to collect on the filter. The dry material attracts water when exposed to air, and becomes soft and sticky; moistened with water, it first becomes soft, and then dissolves fairly rapidly. We can also treat the iron and the tin with nitric acid separately, and then unite the products of the reaction. After evaporation to dryness we find that the stannic oxide, insoluble at first, has passed to the soluble state..

Twice its own volume of concentrated nitric acid is added to the solution. A slightly yellow precipitate is then formed: this is left to settle, and washed two or three times by decantation with nitric acid of 1·2 sp. gr. It is then collected on a hard filter-paper. The mother-liquor does not contain any tin, the compound being completely insoluble in fairly concentrated nitric acid. It is useless to try to eliminate all the iron, either by several washings or by repeated precipitations of the re-dissolved material, since it obstinately retains a quantity of iron which it is difficult to diminish, even with large quantities of solvent. The precipitate is dried in an exsiccator over quicklime, or caustic potash *in vacuo*.

After desiccation it appears in the form of hard resinous lumps; moistened with water, they become disintegrated and decrepitate very slightly; the mass then softens, and eventually dissolves slowly, giving a viscous solution. With only a little water we can obtain a gelatinous product resembling silicic acid. If kept in the exsiccator its solubility gradually diminishes, so that old preparations give up very little tin to the water. The solution contains tin in the form of metastannic acid, as is shown by the following experiments. For the purpose of observing the action of different reagents, it is better to dissolve a portion of the undried precipitate. Nitric acid in excess, dilute sulphuric acid, and oxalic acid; the two latter—even in small quantities—give a precipitate with the solution.

The same result is obtained by boiling the liquid. It is worthy of remark that the primitive solution, which contained a relatively large quantity of iron, is not precipitated by boiling. Further, we can evaporate this solution to dryness without the stannic compound becoming insoluble, while the purified product leaves a soluble residue by desiccation on the water-bath.

Sulphuretted hydrogen precipitates a deep brownish green sulphide from a solution acidulated with a little hydrochloric acid. The sulphide is only deposited slowly. Bichromate of potassium gives a yellow precipitate resembling chromate of lead.

Caustic soda gives a white precipitate very slightly soluble in an excess of the reagent.

Stannous chloride in a slightly acid solution gives a yellow precipitate.

Hydrochloric acid added in excess separates metastannic acid, which is re-dissolved on boiling. In this boiled solution sulphuretted hydrogen precipitates ordinary yellow stannic sulphide. The metastannic chloride has thus passed to the ordinary state.

By avoiding an excess of hydrochloric acid we prevent the separation of the metastannic acid. This solution, kept in the cold, gives a white amorphous precipitate, which is deposited very slowly, on the addition of chloride of cæsium or rubidium.

According to Behrens the two modifications of stannic acid are distinguished in this manner ("Analyse Qualitative Microchimique," p. 63).

As I was not able to obtain soluble metastannic acid in a state of purity, I analysed it such as it was after precipitation with nitric acid. As it persistently retains iron and nitric acid I performed these experiments considering them from the point of view indicated by Van Bemmelen in his researches on the so-called "hydrogels" (*Rev. d. Trav. Chim. des Pays Bas.*, 1888, pp. 91 and 101—103; *Landwirtschaftliche Versuchsstationen*, 1888, p. 90). The metastannic acid was dried in an exsiccator *in vacuo*, over caustic potash or quicklime, and analysed after having been kept under these conditions for varying lengths of time. I estimated the loss of weight by calcination, the amounts of ferric and stannic oxides, and the nitric acid. The separation of the iron and the tin in the calcined residue was effected by heating it with a mixture of soda and sulphur.

By dissolving the melted mass in water we obtain a green liquid, caused by the solubility of the sulphide of iron as shown by Rose (*loc. cit.*, p. 284). On digesting, after having added chloride of ammonia all the iron is deposited. However, the sulphide is not quite pure—it still contains some sulphide of tin; it is therefore necessary to re-dissolve it in dilute hydrochloric acid. Sulphuretted hydrogen is passed through the solution, and the sulphide of tin removed, and the excess of sulphuretted hydrogen driven off by boiling. The iron is then transformed to the ferric state by peroxide of hydrogen, and precipitated by ammonia. The calcined residue represents the ferric oxide. For the estimation of the tin, in some samples, I preferred to treat the green solution with hydrochloric acid, then saturate with sulphuretted hydrogen, and carefully calcine the sulphide of tin, adding a little carbonate of ammonium, to obtain stannic oxide. The filtrate serves for the estimation of the iron. The nitric acid was estimated by Schlœsing's method.

Analyses.

A. The metastannic acid precipitated by nitric acid and washed once with dilute nitric acid by decantation, was dried *in vacuo* over quicklime for five days (*a*), and for fifteen days (*b*).

Matter taken.	Loss by calcination.
a. 0·6562 grm.	0·1448 grm. = 22·1 per cent.
b. 0·5620 ,,	0·0938 ,, = 16·7 ,,

Matter taken.	Nitric oxide.	Nitric acid (N_2O_5).
a. 1·2528 grms.	57·4 c.c. of NO at 18·5° and 760 m.m. =	10·2 per cent.
b. 1·4776 ,,	60·6 c.c. of NO at 18·5° and 760 m.m. =	9·1 ,,

B. The metastannic acid was divided into two parts, which were dried over caustic potash in as perfect a vacuum as possible. The material was in a thin layer.

a. Analysis after five days:—

Matter taken.	Loss by calcination.	Ferric oxide.
0·6576 grm.	0·1414 grm. = 21·5 p. c.	0·0474 = 7·2 p. c.

Calculated for the calcined matter, 9·2 p. c.

	Nitric oxide.	Nitric acid (N_2O_5).
1·8730 grms.	70·7 c.c. of NO at 16° and 767 m.m.	7·8 per cent.

After twenty-two days:—

Matter taken.	Nitric oxide.	Nitric acid (N_2O_5).
0·8684 grm.	29·8 c.c. of NO at 15° and 769 m.m.	7·8 per cent.

b. Second part after twenty-nine days:—

1·8184 grms. 64·2 c.c. of NO at 14° and 760 m.m. 8 p.c.

C. Prepared like A. Analyses after ten, and twenty-five days *in vacuo*:—

Matter taken.	Loss by calcination.	Ferric oxide.
a. 0·5456 grm.	0·1094 grm. = 20·1 p.c.	0·0396 grm. = =7·3 p.c.
b. 0·7742 ,,	0·1342 ,, = 17·3 ,,	0·0574 grm. = =7·4 p.c.

Calculated for the calcined matter, 9·1 and 9 per cent.

To observe the influence of heat on the loss of nitric acid, a sample was kept in a place where the temperature often rose to 35°. The desiccation then took place very rapidly.

a. Analysis after nine days:—

Matter taken.	Nitric oxide.	Nitric acid (N_2O_5).
0·8598 grm.	28·4 c.c. of NO at 13° and 770 m.m.	7·6 per cent.

b. After twenty-two days:—

0·7626 grm.	24 c.c. of NO at 11·5° and 759 m.m.	7·2 ,,

In a portion prepared this summer and kept *in vacuo* several weeks, the proportion of nitric acid went even as low as 4·6 per cent N_2O_5. The loss of weight by calcination was then found to be 20·3 per cent. The material had an opaque appearance, and was hardly soluble at all. Analysis shows that in the exsiccator the material constantly loses water and nitric acid, and also that there is no constant relationship between the ferric oxide and the nitric acid. We may therefore conclude that ferric nitrate, if it exists in the precipitate, is a very unstable compound which is decomposed under these conditions. The proportion of iron is nearly constant after washing with nitric acid, and it is difficult to further diminish it. These results are in accordance with those of M. Van Bremmelen on the "hydrogels" of stannic oxide, which have a composition variable according to the vapour tension of the water, and obstinately retain other substances. In order even to partly dissolve these substances it is necessary to use large quantities of the solvent.

Samples which have been kept a long time in the exsiccator, and have thus lost their water and nitric acid, become very difficulty soluble. The solution of an apparently dry metastannic acid has a strongly acid reaction. By neutralising the solution as accurately as possible with decinormal soda, with phenolphthalein as indicator, all the metastannic acid is precipitated. The result of a volumetric analysis is also well in accord with the estimation of the nitric acid: 1·7760 grm. of the dry precipitate = 37·3 c.c. of 1/10 N soda = 11·3 per cent of N_2O_5. Schloesing's method gives 9·7 per cent.

The neutral point need not be determined very exactly, the colouration of the phenolphthalein disappears slowly on account of the presence of metastannic acid, which already has an acid reaction. The metastannic acid is re-dissolved by adding a slight excess of nitric acid. It seems thus, that this modification of stannic acid requires a certain amount of nitric acid or of ferric nitrate to retain its solubility.

I have also examined how some of the metallic nitrates of the iron group behave with regard to stannic oxide; nitrates of chromium, aluminium, nickel, cobalt, and manganese for example. For 1 grm. of tin I use 3 grms. of crystallised nitrate of chromium or aluminium, and 1 grm. of the nitrates of the other metals. The salts having been added to the tin the whole was treated with nitric acid, and carefully evaporated to dryness. The result found was that the nitrates of chromium and aluminium exercised the same action as ferric nitrate, and that the stannic oxide became soluble. The nitrates of the other metals left it intact. To sum up I must conclude that stannic oxide is rendered soluble only by the nitrates derived from the oxides M_2O_3, while this property does not belong to those of the form MO; also that stannic oxide is then present as a soluble modification of metastannic acid belonging to the class of bodies called "hydrogels."—*Moniteur Scientifique*, December, 1898.

A New Iodide of Tungsten.—Ed. Defacqz.—The author has prepared a new iodide of tungsten, the tetriodide WI_4, by the action of liquid hydriodic acid of tungsten hexachloride. This substance is black and crystalline, slowly changing when in contact with air. It has a density of 5·2 at 18°; it is decomposed slowly by cold water, rapidly by boiling water, giving in both cases the brown oxide and hydriodic acid.—*C. R.*, cxxvii., No. 15.

THE
PREPARATION OF ZIRCONIUM NITRIDES.*

By J. MERRITT MATTHEWS.

THE ammonia derivative of titanium tetrachloride, $TiCl_4 \cdot 4NH_3$, when heated in a current of ammonia gas, yields a nitride of titanium (Rose, *Pogg. Ann.*, xvi., 57; Persoz, *Ann. Chim. Phys.*, xliv., 321). This nitride has been given the formula Ti_3N_4, and has been thoroughly investigated. From this knowledge it was of interest to ascertain if a zirconium nitride could be prepared from its ammonia derivative. The attempt was made, and a corresponding zirconium nitride was obtained.

A portion of the zirconium tetrachloride derivative with ammonia, $ZrCl_4 \cdot 8NH_3$, obtained by passing dry ammonia gas into an ethereal solution of the zirconium salt (*J. Am. Chem. Soc.*, xx., 821), was placed in a porcelain boat and gradually heated to redness in a current of nitrogen in a glass combustion tube. Abundant fumes of ammonium chloride were given off and condensed in the cooler part of the tube; the residue left in the boat was pearl-grey in colour, and in the form of a light powder. On heating this residue in a current of hydrogen, ammonia was evolved, which was conducted into a standardised solution of hydrochloric acid, and thus determined. When this compound was heated in the air it lost weight, and became pure white in colour, passing over into the dioxide, ZrO_2, and the zirconium was estimated in this form.

Analyses.

I. 0·2416 grm. material gave:—
0·0836 grm. ammonia = 0·0688 grm. nitrogen = 28·47 per cent nitrogen.

0·0654 grm. material gave:—
0·0629 grm. zirconium dioxide = 0·0465 grm. zirconium = 71·10 per cent zirconium.

II. 0·2006 grm. material gave:—
0·0691 grm. ammonia = 0·0569 grm. nitrogen = 28·36 per cent nitrogen.

0·2572 grm. material gave:—
0·2469 grm. zirconium dioxide = 0·1827 grm. zirconium = 71·05 per cent zirconium.

These analyses show a close approximation to the formula Zr_3N_8.

	Calculated for Zr_3N_8.	Found. I.	II.
Zirconium	70·82	71·10	71·04
Nitrogen	29·18	28·47	28·36

The residue left after heating this nitride in a current of hydrogen was lead-grey in colour and amorphous; it was soluble in hydrofluoric acid, but proved to be insoluble in the other mineral acids. This appearance and behaviour leave little doubt but that this residue consists of metallic zirconium, the action of hydrogen being to reduce the nitride to the metal with the formation of ammonia.

In the preparation of the pure nitride care must be exercised in excluding all air from the apparatus, otherwise a mixture of the oxide and nitride will be obtained. In the preparation of the sample used for the above analyses, all the air was first driven out by means of a vigorous current of carbon dioxide gas, after which a current of nitrogen was allowed to pass through the apparatus for two hours before the compound was heated.

Zr_2N_3.—This second nitride was prepared by a procedure differing somewhat from that used in the first. Zirconium tetrachloride was placed in a porcelain boat and gradually heated to redness in a current of dry ammonia gas. By this method the ammonia derivative,

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* Contribution from the John Harrison Laboratory of Chemistry, From the *Journal of the American Chemical Society*, xx., No. 11, November, 1898.

$ZrCl_4 \cdot 4NH_3$, was at first formed (*J. Am. Chem. Soc.*, xx., 823). This by the action of the heat was broken down into a nitride of zirconium, together with the formation of ammonium chloride, which was given off in dense fumes and condensed in the cooler part of the tube, leaving the nitride in the boat in the form of a grey amorphous powder. It was somewhat darker in colour than the preceding compound, but resembled it exactly in its behaviour. The nitrogen was estimated by heating the compound in a current of hydrogen, and collecting the ammonia evolved in a standardised solution of hydrochloric acid. By heating another portion in the air it became pure white in colour, increasing in weight, leaving the dioxide, ZrO_2, from the weight of which the zirconium was estimated.

Analyses.

I. 0·2537 grm. material gave :—
0·0478 grm. ammonia = 0·0402 grm. nitrogen = 19·23 per cent nitrogen.

0·2462 grm. material gave :—
0·2707 grm. zirconium dioxide = 0·2001 grm. zirconium = 81·27 per cent zirconium.

II. 0·2217 grm. material gave :—
0·0523 grm. ammonia = 0·0431 grm. nitrogen = 19·42 per cent nitrogen.

0·2546 grm. material gave :—
0·2792 grm. zirconium dioxide = 0·2064 grm. zirconium = 81·05 per cent zirconium.

	Calculated for Zr_2N_3.	Found. I.	II.
Zirconium	81·18	81·27	81·05
Nitrogen	18·82	19·23	19·42

Mallet (*Jsb. Chem.*, clxxxv., 145) obtained a nitride of zirconium by heating the metal in ammonia gas; it is described as a dark grey amorphous powder. A similar product, and one identical in every way with that obtained in this present research, was also prepared by Mallet by heating anhydrous zirconium tetrachloride in ammonia gas. This procedure is exactly similar to that described above; but Mallet made no investigation into the constitution of the compound which he prepared in this manner.

A nitride of thorium has been prepared by Chydenius (*Jsb. Chem.*, 1863, 194) by a procedure identical with that used in the preparation of the first zirconium nitride above described. This nitride of thorium is spoken of as a white amorphous powder, and behaves in a manner very similar to the zirconium compound. Thus the analogy existing between these two elements is once more strikingly manifested.

ON THE SEPARATION OF NICKEL AND COBALT BY HYDROCHLORIC ACID.*

By FRANKE STUART HAVENS.

A QUANTITATIVE separation of nickel and cobalt by a process analogous to that published from this laboratory for the separation of aluminum and iron (Gooch and Havens, *Am. Journ. Sci.*, vol., iv., ii., 416), has been put forward in a recent paper by E. Pinerùa (*Gaz. Chim. Ital.*, vol. xxvii., 56). The process may be described briefly as follows:—The hydrous chlorides of nickel and cobalt (0·3—0·4 grm.) are dissolved in a little water, and to the solution are added 10 to 12 c.m.^{3} of aqueous hydrochloric acid, and 10 c.m.^{3} of ether, and the whole, contained in a little beaker surrounded with water and ice, is saturated with gaseous hydrochloric acid. The cobalt, which remains in solution, is decanted off and the yellow insoluble nickel chloride washed with a previously prepared solution of ether saturated with hydrochloric acid gas at a low temperature. The nickel is determined by known methods, preferably as the sulphate. The author claims very precise results for the process, but gives no experimental proof of his work. Previous to the appearance of this paper my experiments upon the solubility of nickel chloride in an ether-hydrochloric acid solution, such as used in our process for the separation of aluminum and iron, which is practically the same in proportions as that used by Pinerùa to effect precipitation, had shown that, while nickel chloride is somewhat insoluble in such a mixture, the degree of insolubility is not sufficient for a quantitative separation. Since the appearance of Pinerùa's work I have been over the ground again, and have reached the same conclusions as before, as shown in the following experiments.

When a solution of 0·2 grm. of nickel chloride (free from iron and cobalt) in 7 c.m.^{3} of aqueous hydrochloric acid was saturated with hydrochloric acid gas at a temperature of −2° C. (obtained by immersing the container in a mixture of ice and salt) no precipitation resulted. When, however, an equal volume of ether was added and the whole was again saturated with hydrochloric acid gas a yellow precipitate formed, while the supernatant liquid still remained of a deep green colour. The solution was filtered quickly through asbestos in a filter crucible, and the clear filtrate after evaporation with sulphuric acid was electrolysed. The metallic deposit of 0·0020 grm. proved to be pure nickel; for when dissolved in nitric acid it gave no test for iron with potassium sulphocyanide or ferrocyanide, and neither the apple-green hydroxide nor the black sulphide, prepared by the usual methods, showed any trace of cobalt in the borax bead. It is obvious, therefore, that nickel chloride is not fully precipitated under these conditions and that the green colour of the solution is due to nickel in solution and not to traces of iron, as Pinerùa has supposed (*loc. cit.*) A second experiment similar to the first showed a solubility of the nickel chloride represented by 0·0018 grm. of metallic nickel. It is evident, then, that the solubility of nickel chloride in this mixture of aqueous hydrochloric acid and ether thoroughly saturated with hydrochloric acid gas is not far from an amount represented by 0·0020 grm. of metallic nickel for every 14 c.m.^{3} of solution.

Still another experiment, in which nickel chloride representing 0·0020 grm. of metallic nickel was treated with 14 c.m.^{3} of the ether-hydrochloric acid solution and the whole saturated for one hour at a low temperature with hydrochloric acid gas without precipitation, showed the same thing.

When the nickel chloride remaining on the asbestos was washed with about 40 c.m.^{3} of a mixture of equal parts ether and aqueous hydrochloric acid saturated with hydrochloric acid gas, the washings evaporated with sulphuric acid and treated by the battery gave a deposit of metallic nickel weighing 0·0027 grm.—an amount proportionately less than that found in the filtrate proper.

Although employing a mixture of aqueous hydrochloric acid and ether saturated with gaseous hydrochloric acid for the precipitation, Pinerùa has advised the use of pure ether saturated with gaseous hydrochloric acid for the washing. In my experiments with such a mixture I find that in it the hydrous nickel chloride is practically insoluble and that 30 c.m.^{3} of the washings of the precipitated chloride with such a mixture gave no deposit of nickel by the battery. It seemed possible, therefore, that by reducing the water present to the lowest possible amount necessary to dissolve the chlorides to be treated the precipitation of the nickel might be made more complete. The experiments of the following table were made to put this idea to the test.

Solutions of the pure chlorides of nickel and cobalt, carefully purified and freed from other metals and each other, were, after conversion to the form of the sulphate, standardised by the battery. Weighed portions of these solutions were taken in a small beaker, evaporated to dry-

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* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, 1898, vol. vi., p. 396.

ness, the dry salts dissolved in as little water as possible (about 1 c.m.^{3}), 10 to 15 c.m.^{3} of ether added, and the whole saturated with hydrochloric-acid gas, the beaker being meanwhile immersed in running water and cooled to about 15° C. When saturation was complete the precipitated chloride was caught on asbestos in a filter crucible, washed thoroughly with a previously saturated solution of ether, dissolved in water, evaporated with sulphuric acid and determined as metallic nickel by the battery. The cobalt in the filtrate was recovered by evaporation and electrolysis in like manner.

Experiments 1, 2 and 3 of the accompanying table show that by this process the nickel is thrown down quantitatively, and experiments 2 and 3 show that in the presence of a few milligrms. of the cobalt salt the separation of a small amount of nickel is sharp. The residue of nickel in these experiments gave no test for cobalt with the borax bead. When, however, the cobalt is present to the amount of a few centigrms. as in 4, 5, and 6, the precipitated nickel chloride, which forms a hard mass, includes the cobalt salt, so that even a large quantity of washing solution (100 c.m.^{3} was used in experiment 6) cannot remove it.

	Nickel taken as the hydrous chloride.	Nickel found.	Error.	Cobalt taken as the hydrous chloride.	Cobalt found.	Error.
1.	0·0068	0·0066	—0·0002	—	—	—
2.	0·0090	0·0090	0·0000	0·0030	—	—
3.	0·0090	0·0091	+0·0001	0·0123	0·0127	+0·0004
4.	0·0469	0·0490	+0·0021	0·0700	—	—
5.	0·0468	0·0503	+0·0035	0·0700	—	—
6.	0·0472	0·0493	+0·0021	0·0700	—	—

From the experiments described it is obvious that the process as proposed by Pinerùa will not give a complete precipitation of the nickel chloride. Nickel chloride is, however, practically insoluble in pure ether saturated with hydrochloric acid gas and can be separated from small quantities of the soluble cobalt salt in that medium. In the presence of even a few centigrms. of the cobalt chloride, however, the process is not practicable on account of the inclusion of the cobalt by the massive nickel chloride. It is possible that by repeated solutions and reprecipitations the nickel salt might be sufficiently freed from the cobalt, but the process must naturally be long and tedious.

In closing the author wishes to express his gratitude to Professor Gooch for kind suggestions.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 1st, 1898.

Professor Dewar, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. Samuel William Allworthy, The Manor House, Antrim Road, Belfast; John Frank Blackstraw, Holly Bank, Marton, Chelford, Cheshire; Henry Cort Harold Carpenter, 109, Banbury Road, Oxford; Frank Cope, 30, Leeds Road, Dewsbury; Thomas James Cozens, The Grammar School, Middleton-in-Teesdale, Co. Durham; Samuel Godfrey Hall, 19, Aberdeen Park, Highbury, N.; Thomas Anderson Henry, 37, Chelsea Gardens, S.W.; Thomas Luxton, 4, Cavendish Square, Margaret Street, Hull; James Roberts, jun., 43, Great Western Road, Glasgow; Frederick William Skirrow, Graystongill, Bentham, Lancaster; Charles Emerique Szarasy, 19, Weymouth Street, Portland Place, W.; Thomas Wilson Wormell, 184, Burrage Road, Plumstead, S.E.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected.

Hugh Poynter Bell, B.A.; Reginald Arthur Berry; Walter Birkett; Thomas Henry Boardman, B.A.; Marston Taylor Bogert, A.B., Ph.B.; Arthur Brooke, B.A.; Johannes Christian Brünnich; John Paul de Castro; Charles Robert Carroll; David Leonard Chapman, B.A.; William Samuel Crouch; Alfred V. Cunnington, B.A.; W. Brown Davidson, M.A., Ph.D.; Samuel Dickson; Francis Alfred Drake, B.Sc.; James Edward Ferguson; Edward Gardner; John Naish Goldsmith, B.Sc., Ph.D.; E. B. Hadley; Alfred Hartridge, B.A.; John Haworth; Alexander Garden Hendry; George W. F. Holroyd, B.A.; Walter Howe; Thomas Hill-Jones; Benjamin Jordan-Smith; Reginald Arundale Kay; John Charles Mascarenhas; William Lash Miller, B.A., Ph.D.; Thomas Arthur Nightscales; William Pollard, B.A., Ph.D.; John Armstedt Ray, jun., B.A.; Edmund Milton Rich; Gilbert Rigg; Henry John Rofe, B.A.; Henry J. S. Sand, Ph.D.; Richard Seligman; George Senior, B.A.; Samuel Smiles, jun., B.Sc.; Basil Steuart; Ambrose Walton; Frederick Louis Wilder; Charles William Tuthill Woods; John Henry Young, B.Sc.

The following papers were read:—

144. "*The Oxidation of Polyhydric Alcohols in presence of Iron.*" By Henry J. Horstman Fenton, M.A., and Henry Jackson, B.A., B.Sc.

In continuation of the study of the influence of ferrous iron on the oxidation of various hydroxy-compounds, the authors are engaged in investigating the behaviour of various alcohols, and the present communication gives an account of the results which, so far, have been obtained.

The monhydric alcohols (methylic, ethylic, propylic, isopropylic, and amylic), under the conditions employed, give entirely negative results either in presence or absence of iron. But in the case of all the polyhydric alcohols examined (ethylene glycol, glycerol, erythritol, mannitol, dulcitol, and sorbitol), it is found that the presence of ferrous iron exerts a remarkable influence on oxidation by means of hydrogen dioxide. In the absence of iron practically no change is produced, but, in its presence, very considerable rise of temperature occurs in all cases, and the alcohol is vigorously oxidised.

Ethylene glycol yields glycollic aldehyde, but apparently no glyoxal. With glycerol the product appears to be glyceraldehyde with little or no dihydroxyacetone. From erythritol a product yielding erythrosazone is obtained, and mannitol gives mannose. The yields, generally, are remarkably good as compared with those obtained by oxidation with nitric acid, &c., and in this way it is easy to obtain mannose directly from mannitol without first preparing the hydrazone. The authors are attempting to isolate tetrose in a similar way.

As in the case of tartaric acid, it is found that certain of these polyhydric alcohols may be similarly oxidised by atmospheric oxygen in presence of ferrous iron and of sunlight.

145. "*The Occurrence of Hyoscyamine in the Hyoscyamus Muticus of India.*" By Wyndham R. Dunstan and Harold Brown.

The authors find that the stem and leaves of the Indian *Hyoscyamus muticus* contain about 0·1 per cent of hyoscyamine, and that the alkaloid can be extracted in a pure state from this plant more readily than from ordinary henbane. The plant is fairly abundant in the Punjab and Beluchistan, and is likely to prove of value both as a drug and as a source of hyoscyamine.

Discussion.

Professor Dunstan, in reply to Mr. Groves, Mr. David Howard, and Mr. Page, said it was possible that age and climate might have some influence in changing the hyoscyamine and forming other mydriatic alkaloids. There was every reason to believe that the physiological action of the drug was principally due to the alkaloid it contains, and not to any other constituent.

Dr. W. H. Perkin, F.R.S., then took the chair, and the following paper was read:—

146. "*The Comparative Colour of the Vapour of Iodine in Gases at Atmospheric Pressure and in a Vacuum.*" By James Dewar, LL.D., F.R.S.

Recently, having had occasion to compare iodine with other substances as a means of obtaining vacua in the construction of vessels used for the storage and manipulation of liquid air in low temperature research, some facts about the behaviour of the vapour of iodine have been observed which deserve to be recorded. Pure iodine in the solid state is usually stated to be perfectly opaque to light, but this is not the character of iodine distilled and condensed on a surface of glass at temperatures between −180 and −190 in vacuum test tubes or bulbs by the use of liquid air. Under such conditions it is easy to get transparent films of iodine of varying grades of thickness showing brilliantly the colours of thin plates by reflection, and to keep them permanently as long as the low temperature is maintained. The first addition of liquid air to the vacuum bulb or test tube containing excess of solid iodine causes instant precipitation of an opaque film, but this can be avoided by cooling the iodine, which has been caused to sublime to the lower part of the outer test tube or bulb, by a preliminary treatment with a little solid carbon dioxide.

In this condition, when the inner surface of the vacuum vessel is cooled with liquid air, the iodine can only deposit from an atmosphere of great tenuity, and when a given thickness of deposit is reached, any increase can be stopped by removing the vessel from the liquid carbon dioxide and placing it in liquid air. In the same way films of other substances can be deposited, which may be useful in the examination of many physical problems. Stas says that pure iodine gives no visible vapour at the ordinary temperature, but this is contrary to the author's experience. Samples of iodine, obtained from cuprous iodide, from iodoform, and from solution of iodine in potassium iodide, and in sufficient quantity to ensure saturation, gave, in half-litre flasks, a visible colour to the atmosphere at the ordinary temperature. When, however, a similar flask containing the same iodine was exhausted of air, the colour of the atmosphere was markedly less, and this distinction remained even when the flasks were heated side by side in a water bath. If the iodine vapour diffused into an atmosphere of carbon dioxide, hydrogen, or oxygen, in similar flasks, instead of into air, the colour remained the same; but in all cases it was much more marked than in one from which the gaseous atmosphere, other than iodine, had been in great part removed by the air pump. No change in the mode of filling the air and vacuum flasks made the difference in colour disappear, although a dozen flasks have been filled from time to time. No change in the character of the results was effected by subliming the iodine from anhydrous baryta, and keeping it in flasks for months with excess of the latter, nor was any apparent difference produced when the flasks containing the baryta were repeatedly heated at the boiling point of water. This seems to prove that neither water vapour nor hydrogen iodide has anything to do with the cause of the difference in colour of the iodine vapour in the air and vacuous flasks. It is not necessary to use flasks, as two lengths of glass tubing, an inch or less in diameter and a foot or more in length, when heated side by side in a steam or water bath, show the difference of colour.

To obtain an approximate value of the tension of the saturated vapour of iodine at about the ordinary temperature, a Rankine formula of two terms was calculated, taking the known pressure at 58·1° as 4·9 m.m. and that at 113·8° as 87 m.m. These gave:—

$$(1)\ \log P = 9{\cdot}3635 - 2872/T \text{ m.m.}$$

If, however, the tension at 85° and 114·1° are selected for calculation,—

$$(2)\ \log P = 10{\cdot}0392\ 3137/T \text{ m.m.},$$

where T is the absolute temperature. From formula (1) the tensions in m.m. of mercury at 0° and 11° are respectively 0·07 and 0·18. The weight of iodine in a litre would thus become about 1 and 1·94 m.grms. at 0° and 11° respectively. In order to check this calculation, the quantity of iodine required to saturate a litre of dry air at 0° and 11° was determined by passing a slow current of air over a column of the substance, and subsequently absorbing the iodine from the saturated air by passing it through a caustic potash solution. The alkaline solution, after acidifying, was titrated with sodium thiosulphate. The results of the experiments were as follows:—

	M.grms. per litre.	Pressure in m.m. of mercury.
0°	0·24	0·017
11°	1·25	0·087
30°	4·70	0·358

In each case, the calculated tension is less than that deduced from the first vapour pressure equation. The values approach those given by Arctowski (*Zeit. Anorg. Chem.*, 1896, vol. xii., 427) as a deduction from his experiments on the volatilisation of iodine. From this, it would follow that the second equation for the tension is the better. In the liquid state, the tensions are well represented by (3) $\log P = 7{\cdot}924\ 2316/T$ m.m. From formula (2), the molecular latent heat of solid iodine is 14430 units, and for the liquid condition from (3) the value is 10653. The experimental value of the latent heat of liquid iodine given by Favre is 6000 units. From this, it would follow that the latent heat of volatilisation requires to be re-determined. It is interesting to observe that the number of heat units required to dissociate the molecule of iodine is 28500, or roughly, twice the calculated latent heat of the solid.

The various experiments recorded lead to the conclusion that the phenomenon is a real one, although some factor that has been neglected may explain it; at any rate, it is difficult to avoid getting the result. Assuming it be true, its explanation then remains to be considered. It is well known that the vapour pressure in a vacuum is often greater than in air at atmospheric pressure. On the other hand, Professor J. J. Thomson, in his work entitled "Application of Dynamics to Physics and Chemistry," p. 169, discusses this very question. He shows that the effect of the pressure of an inert gas must be to raise the vapour pressure of a substance diffusing into it above that produced by the diffusion of the same substance into a vacuous space. Taking the equation which he there developed as being applicable to iodine, the difference between the two conditions of pressure should amount to $\frac{1}{440}$ of the whole. Now the question arises whether this amount is sufficient to explain the difference of colour or whether it is necessary to bring in other factors which may operate, such as solution of solids in gases under pressure, dissociation, or want of equilibrium. Further experiments will be required before a definite answer can be given.

Hannay and Hogarth first showed that alcohol vapour above its critical point, and therefore at a pressure above 60 atmospheres, can dissolve solids like potassium bromide or iodide, and Cailletet, a little later, found that liquid carbon dioxide was dissolved by air under high compression. Dr. Villard has recently made a series of experiments on the same subject, in which he proves that bromine and iodine dissolve in air or oxygen under high compression. He says: "L'iode se dissout egalèment en quantité sensible dans l'oxygène, mais le phénomène n'est bien visible qu'a partir de 100 atmosphères et dans des tubes de 5 millimetres de diametre au moins."

The experiment exhibited would appear to show that the pressure of one atmosphere is sufficient to produce a sensible difference of colour in the case of iodine vapour diffused in air and in a vacuum. For the present, it may be regarded as a lecture illustration of the rapidity of volatilising iodine in an air space as contrasted with a vacuous one.

Discussion.

Dr. Thorpe thought that the phenomenon which the President had brought to the notice of the meeting was highly interesting and suggestive. It seemed to him, after watching the experiment shown to them during its whole course, that the character of the colour of the resulting vapours was so markedly different as to lead to the inference that something more than a mere dilution of colour due to an actual difference in the amount of vapour present had occurred. He could not help comparing the phenomenon with the well-known difference in colour of various solutions of iodine in alcohol, carbon disulphide, chloroform, &c., and thinking that molecular dissociation was taking place. Perhaps in this connection it might be worth while to make a comparative spectroscopic study of the vapours in the two conditions.

Professor F. D. Brown said that he, too, had remarked the much browner colour of the iodine vapour in the vacuous tube. Remembering the fact that iodine in brown solutions is in a different molecular condition from that in violet solutions, it seemed probable that the vapours in the two tubes were also in different molecular conditions.

With regard to the suggestion that the iodine was in some way dissolved in the gas, he stated that one of his students in New Zealand had ascertained that equal volumes of different gases at the same temperature and pressure took up exactly equal quantities of iodine, whereas it was probable that if iodine dissolved in a gas as a solid dissolves in a liquid differences in solubility would have been found.

Mr. Elworthy, in reference to the solubility of solids in gases at temperatures above their critical points, and under pressure, said that when in Bombay he gave instructions for some vulcanised rubber to be placed in a vessel with carbon dioxide at about 5 or 6 atmospheres pressure; instead of this about 5 pounds of the gas were introduced into a vessel usually employed to contain 15 pounds of liquefied carbon dioxide. At temperatures below the critical point a certain amount of liquefied gas would have been present, but as the temperature was between 87° and 90° F., the gas was in the condition of a vapour under pressure. On opening the vessel and allowing the gas to escape, it was found that practically all the sulphur had been dissolved out of the rubber, the surface of which was covered with a thin crust of sulphur crystals.

Mr. L. M. Jones asked whether any attempt had been made to determine the actual concentration of the iodine in the two cases; and also whether the apparent solubility of a solid in gas at high pressure might not be actually due to the increase of vapour pressure predicted by Professor J. J. Thomson.

Dr. Travers pointed out that the critical phenomena observed when the air confined over liquid carbon dioxide was compressed at constant temperature could not be produced by conditions similar to those which were present in the case of the iodine and air. When air was compressed in contact with any liquid, it dissolved and produced a mixture of constantly decreasing critical temperature. Consequently, supposing that sufficient air were present, it should in any case be possible by exerting sufficient pressure to produce a mixture whose critical temperature was the temperature of the experiment. The phenomenon could have nothing to do with the solution of the solid or liquid in the gas.

Dr. Forster inquired whether iodine had been imprisoned in atmospheres other than a mixture of nitrogen and oxygen. If, as was suggested, the phenomenon in question is a case of solution, differences in appearance similar to that subsisting between solutions of iodine in alcohol and in carbon disulphide, might be expected in tubes containing iodine enclosed with various inert gases.

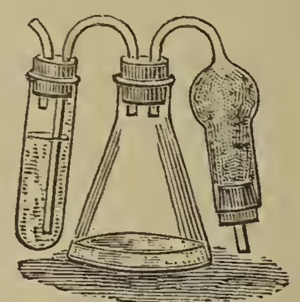
The President, in reply, said that the spectroscope had not been used in his experiments, and bearing in mind the character of the absorption spectrum of iodine, he anticipated it would be difficult to obtain any information as to the character of the phenomenon by its employment. The possibility of dissociation had not escaped attention, having been mentioned in the paper. All that he could say was that at present he could not specifically state that the difference in the behaviour of iodine under the two conditions was due to one or other of the possible causes to which he had referred. Iodine enclosed in tubes containing gases such as carbon dioxide, nitrogen, hydrogen, and oxygen gave appearances indistinguishable from those observed in similar tubes containing air.

CORRESPONDENCE.

SIMPLE APPARATUS FOR THE ESTIMATION OF CARBON DIOXIDE.

To the Editor of the Chemical News.

Sir,—In the Chemical News for December 16 (vol. lxxviii., p. 293), Mr. W. H. Barker describes and figures a "Simple Apparatus for the Estimation of Carbon Dioxide."



May I be allowed to remark—

1. That this apparatus only differs from the well-known apparatus of Bunsen by the shape of the flask; and,
2. That this modification has already been described by me in my "Traité de Chimie Analytique Minerale, Qualitative and Quantitative," vol. ii., p. 991, with a second modification, which consists in replacing the bulb tube for the acid with a small test-tube; the manipulation with this seems to be more convenient. See the accompanying figure extracted from my book.—I am, &c.,

Dr. L. L. de Koninck.

NOTICES OF BOOKS.

Some Interesting Soil Problems. By Milton Whitney. Reprint from *Year-book of Department of Agrculture for* 1897.

It is found in the United States that, as a rule, soil problems in the extreme West are simpler and easier to study than anywhere else in the country; the soils themselves are more uniform in their texture, and there is less variation from the normal climatic conditions. When rainfall is scanty, as in this district, the rocks are more apt to disintegrate with comparatively little decomposition; this disintegration has in most cases reached to a considerable depth, so that there is seldom a difference between the soil and the subsoil, as there is in the moister climate of the East.

Some of these soils absorb water so readily, and lose it by evaporation so slowly, and yet supply the plants so regularly and abundantly, that they can stand long periods of drought without the crops suffering to any noticeable extent.

In the great wheat areas in the northern part of California, and other adjacent places, the soils produce fine crops of wheat without irrigation; they are strictly summer crops, and the soils have the power of retaining the winter rains and giving up the moisture when it is needed, and, as the rainfall is but from 13 to 18 inches per annum, it is considered very doubtful, or wholly improbable, that any of the water leaks away and runs off in the country drainage. If this power of retaining water can be imparted to other soils, and especially to those of the East, it will be of very great value and importance to the farmer.

The first question to solve is the distribution of the rainfall and the average depth of wells,—that is, the depth to standing water; another question which can be determined experimentally is, What is the minimum quantity of water required by these soils to enable them to support a crop? It is not sufficient that a soil should be very retentive of moisture, but it should also conserve it, losing very little by evaporation, but at the same time the water must move rapidly up to the roots of the plant; it is thus not only the water capacity of the soil, but also its ability to supply this water to the plants, that determine its agricultural value.

CHEMICAL NOTICES FROM FOREIGN SOURCES

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvii., No. 15, October 10, 1898.

Preparation and Properties of Calcium Nitride.—Henri Moissan.—If a piece of crystalline calcium is suspended in an atmosphere of pure dry nitrogen, and the temperature gradually raised, the metal slowly begins to absorb the gas, and its white colour changes to yellow. As the temperature increases, the colour deepens. At a red heat the combination takes place with incandescence; the calcium burning in the nitrogen gas, and the absorption taking place very rapidly. The best method of preparing calcium nitride is to place the crystalline calcium in a nickel boat; the boat being placed in a tube of the same metal. A current of pure dry nitrogen is then passed through the apparatus. The nitride thus formed is in the form of little transparent brownish yellow crystals having a density of 2·63 at 17°. It corresponds to the formula N_2Ca_3; it unites easily with chlorine, bromine, iodine, oxygen, sulphur, and phosphorus, and is decomposed by carbon at a high temperature. With anhydrous alcohol it gives ammonia and calcium ethylate; and it decomposes cold water, giving ammonia.

Crystalline Tungsten Dioxide and Tungsto-Lithium Tungstate.—L. A. Hallopeau.—Crystalline dioxide of tungsten can be prepared from paratungstate of lithium; the latter, unlike the paratungstates of potassium and sodium, being capable of complete reduction by hydrogen at a red heat. The dioxide obtained is a brown powder composed of very small crystals belonging to the regular system, and having a formula WO_2. In order to obtain from paratungstate of lithium a tungsten bronze, the lithium salt must be reduced by an agent other than hydrogen. It has already been found that blue quadrilateral plates are formed by the action of tin on lithium tungstate. The author has repeated this preparation, and made an accurate analysis of the product formed. The analysis confirms the formula $Li_2W_5O_{15}$, which can be written $Li_2O.WO_3+WO_2.3WO_3$.

Thermometric Study of the Suboxide and the Peroxide of Sodium.—M. de Forcrand.—The author has found the heat evolved when the three oxides of sodium Na_3O, Na_2O_2, and Na_2O are decomposed by water. (1) The difficulty in the case of the suboxide Na_3O is owing to the violence of the reaction; the determination must be done in the absence of air, to prevent the cooled hydrogen from inflaming. The mean of two experiments gives 97·78 calories as the heat evolved during this reaction. (2) The dioxide can be dissolved directly in the water of the calorimeter; the chief difficulty being that the oxygen is not all evolved, but is partially absorbed to make peroxide of hydrogen; it is better therefore to dissolve the dioxide in dilute hydrochloric acid; 119·79 calories is the number found. (3) 19·39 calories is the number for the decomposition of the protoxide Na_2O.

On the Combinations of Lithium Chloride with Methylamine. — H. Bonnefoi. — Pure anhydrous lithium chloride absorbs methylamine gas (as it does ammonia), forming with it three successive combinations, of which the dissociation and heat of formation have been studied by the author. To render the salt porous and voluminous, dry ammonia gas is passed over it, and subsequently completely expelled by heat in a current of dry nitrogen. During absorption, the chloride swells up, and remains in this condition, which is the most favourable for the absorption of methylamine. The combination $LiCl+CH_3NH_2$ is formed above +65°. $LiCl+2CH_3NH_2$ is produced between +40° and +65°, and $LiCl+3CH_3NH_2$ below 40°. The heats of solution in water of methylamine gas and of these three substances having been determined, the following equations are deduced:—

1. $LiCl(sol.)+CH_3NH_2(gas)=$
$=LiCl+CH_3NH_2(sol.)+13·82$ cal.
2. $LiCl(sol.)+2CH_3NH_2(gas)=$
$=LiCl+2CH_3NH_2(sol.)+25·88$ cal.
3. $LiCl(sol.)+3CH_3NH_2(gas)=$
$=LiCl+3CH_3NH_2(sol.)=36·69$ cal.

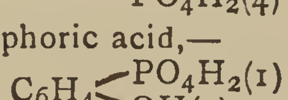
It follows from this research that the formula of Clapeyron is perfectly applicable to the dissociation of these compounds.

A Di-iodine Derivative of Quinoline.—C. Istrati.—So far no general method has existed for introducing halogen atoms into ring compounds containing nitrogen, such as pyridine and quinoline. The author describes a method by which these iodine derivatives may be easily prepared. Taking the case of quinoline:—Quinoline sulphate, dissolved in excess of sulphuric acid, is treated with iodine for several days; the degree of substitution which occurs depending on the quantity of iodine introduced and the temperature to which the mixture is subjected. On pouring the product into much water, a brownish deposit is obtained, and, finally, a small quantity of a white deposit. The precipitate is treated with potash and then extracted with alcohol. Crystals of a new substance, the di-iodine derivative of quinoline, are obtained. Analysis gives it the formula $C_9NH_5I_2$. There are also found —in a portion less soluble in alcohol, but soluble in chloroform—derivatives containing more than two atoms of iodine in the molecule. The white second precipitate crystallises from alcohol and corresponds to the formula C_9NH_6I. The production of these substances is also accompanied by a sulphonated derivative of quinoline.

Phenyl- and Phenylene-phosphoric Acids.—P. Genvresse.—The author gives a description of the preparation and properties of phenyl-phosphoric acid,—

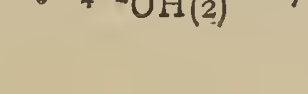
$$C_6H_5.PO_4H_2;$$

phenylene-diphosphoric acid,—



$$C_6H_4 \begin{matrix} \diagup PO_4H_2(1) \\ \diagdown PO_4H_2(4) \end{matrix} ;$$

and oxyphenylphosphoric acid,—



$$C_6H_4 \begin{matrix} \diagup PO_4H_2(1) \\ \diagdown OH(2) \end{matrix} ;$$

These are crystalline substances obtained by the action of phosphoric anhydride upon phenol and polyatomic phenols. respectively.

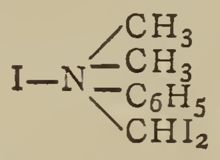
Volumetric Estimation of Ethyl Aldehyd.— X Rocques.—This paper describes the volumetric estimation of ethyl aldehyd in dilute alcoholic solution (*e.g.*, as it occurs in brandies). The method depends on the reaction between acid sulphites and aldehyds. This reaction, in the case of solutions containing only 1 per cent of aldehyd, is not complete in the cold for several hours. A normal solution of sodium acid sulphite is made, and a known volume added to the alcoholic solution of aldehyd. After standing, this is titrated with normal iodine solution, and hence the percentage of aldehyd calculated.

Thermic Constants of Isoamylmalonic Acid.— G. Massol.—The heats of solution in water of this acid and its neutral potassium salt are given; also the heat of neutralisation of the acid by potash, and the results compared with the numbers obtained for its isomer, suberic acid.

——

Bulletin des Travaux de la Société de Pharmacie de Bordeaux, July, 1898.

Compounds obtained with Iodoform and the Tertiary Aromatic Amines.—G. Denigès.—The author was led to undertake these experiments when attempting to generalise Caro's reaction by which fuchsine was obtained by heating large quantities of iodoform with aniline. He found that the secondary and tertiary amines behaved in the same manner as the primary ones, and often gave better results, especially in the case of dimethylaniline. The action of heat on iodoform is always the cause of the liberation of iodine, and it was thought probable that the production of these coloured derivatives might be preceded by the dislocation of the iodoformic molecule, with the fixation on the amines of the products of this splitting up. Such products, both definite and stable, were obtained with the tertiary amines. Under the influence of sunlight the dissolved iodoform is decomposed into free iodine and an iodised residue, which at once combine with the amine, giving an iodo-substituted quaternary iodide of ammonium.



$$I{-}N\begin{array}{l}CH_3\\CH_3\\C_6H_5\\CHI_2\end{array}$$

Analogous compounds have been obtained with di-iodoform.

The Use of Binoxide of Lead in Analysis; Application to Urines and Fermented Liquors.—A. Loubiou.—The author has applied the oxidising properties of binoxide of lead, the intensity of which can be varied according to the neutrality or acidity of the surrounding medium, or its absorbent properties for simplifying and bringing into practical form the estimation of certain principles of urine and fermented liquors. The method of detecting and estimating albumen in urine is to add one drop of phenolphthalein to 10 c.c. of the sample, then add drop by drop normal soda until the colour is slightly pink, add to the liquid 1 to 1·5 grms. of binoxide of lead, shake well for a minute, and filter; a few drops of Tanret's reagent is added to the solution, which then takes its original colour. On boiling, if albumen is present, a cloudiness or a precipitate is formed according to the quantity present. The author is convinced by the results obtained, that binoxide of lead does not attack the albumenoid matter in a neutral solution, while it allows of the complete clarification of the liquid; several comparative results are given to prove this.

September, 1898.

The Use of Binoxide of Lead in Analysis; Application to Urines and Fermented Liquors.—H. Loubiou. —For the estimation of the reducing matters of cider, place 10 c.c. of cider in a 100 c.c. flask with sufficient normal soda to neutralise it, add 0·2 c.c. of acetic acid and make up to 100 c.c., shake well, then pour the whole into a 150 c.c. flask, and add 2 grms. of binoxide of lead; cork up and shake well for a minute, then filter; in the flask used for the reduction place 25 c.c. of Bonnan's solution and bring up to boiling point, then pour in four or five drops of the filtered liquid and boil again; repeat this until a yellow colour appears, then add only two drops at a time; this must be continued until a blackish red colour appears, which indicates the end of the reaction. Let n be the number of cubic centimetres of the filtrate used and T the titration value of the Bonnan's solution; 1 c.c. of filtrate corresponds to T/n and 1000 c.c. to $T/n \times 1000$, but the cider was first diluted to 1 in 10, so its real value in glucose will be $T/n \times 1000 \times 10$. In a large number of experiments most satisfactory results have been obtained by this method. The same method is applied to beer and urines with equal success.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Artificial Manures.—Can any reader tell me the name and price of the three best books on the manufacture of artificial manures; what are the percentages of potassium chloride, potassium sulphate, salt, and iodine in (1) dry sea-weed, and (2) in kelp? Also the name and address of any firm or private person in Germany or London who could supply me with tubes of the nitrifying organisms of the soil?—J. H.

MEETINGS FOR THE WEEK.

TUESDAY, Jan. 3rd, THURSDAY, 5th, SATURDAY, 7th.—Royal Institution, 3. (Christmas Lectures). "On Astronomy," by Sir Robert Stawell Ball, F.R.S., &c.
WEDNESDAY, 4th.—Society of Arts, 7. (Juvenile Lecture). "Hands and Feet," by Prof. F. Jeffrey Bell.

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